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Structural and synthetic studies of transition metal complexes with unsaturated organic ligands

STRUCTURAL AND SYNTHETIC STUDIES OF TRANSITION METAL COMPLEXES WITH UNSATURATED ORGANIC LIGANDS

by

I.D. WILLIAMS

A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Bristol.

The University,
Bristol

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MEMORANDUM

The research described in this Thesis was conducted in the Department of Inorganic Chemistry at the University of Bristol, between October 1980 and September 1983. Unless otherwise acknowledged, the results presented are the Author's own work and they have not been used previously in any other dissertation.

I.D. Williams
School of Chemistry,
Bristol 1985.

To my family and friends.

ACKNOWLEDGEMENTS

My thanks go to Drs. A.G. Orpen and M. Green for their constant advice, encouragement and support throughout the course of this project and their patience with me at its end.

I am grateful to my co-workers who supplied me with crystals; Dr. R.G. Beevor, Dr. S.R. Allen and especially Dr. C.J. Schaverien.

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Finally I would like to thank Ms. P. Bianconi for proof-reading the thesis and the S.E.R.C. for the award of a research scholarship.

SUMMARY

Section 1 of this Thesis describes the organometallic chemistry of a series of mono-nuclear molybdenum complexes containing the fragment $[Mo\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, from a structural and synthetic standpoint.

Section1.1. discusses the chemistry of the cationic alkyne complex $[Mo(HCCBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (I), including its reaction with nucleophilic reagents to form η^1-acetylide, η^1-vinyl and η^2-vinyl complexes, with structure determinations on (I) and examples of all of the above species.

Section 1.2 describes the structure of the alkylidyne complex $[Mo(CCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (VI), which may be formed by treatment of (I) with hydride. Evidence for the involvement of a η^2-vinyl complex as an intermediate in the reaction is presented.

Section 1.3 presents a reinvestigation of the protonation of (VI) with both $[HBF_4]$ and $[CF_3COOH]$ and includes structure determinations of the alkylidyne-hydride complex $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo\{P(OMe)_3\}_2(\eta^1\text{-}OCOCF_3)(CF_3COOH)(\eta\text{-}C_5H_5)]$. The products of the reaction of (VI) with the electrophiles (TCNE) and $[CO(CF_3)_2]$, $[Mo(CCH_2Bu^t)(\eta^2\text{-}C_2(CN)_4)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ and $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_3\{COH(CF_3)_2\}_2]$ respectively, are structurally characterised.

Section 1.4 describes a variety of synthetic routes to neutral and cationic vinylidene complexes with structural analyses of two of the neutral species $[Mo(C{=}CHBu^t)$-

$\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I]$ (XII), and $[Mo(C{=}CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)Br]$. The protonation of the (XII) to yield a cationic alkylidyne complex is reported.

Section 2 comprises a series of structure determinations, (I) - (VII), resulting from the reaction of 3,3-dimethylcyclopropene with a variety of dimetallic complexes.

The product from the reaction of 3,3-dimethylcyclopropene with $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$, the μ-allylidene complex $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(\eta\text{-}C_5H_5)_2]$ reacted with $[HCCBu^t]$ to give $[Mo_2(CO)_2(\mu\text{-}CMe_2CH.CH.CH.CBu^tCO)(\eta\text{-}C_5H_5)_2]$ (I) and [MeCCMe] yielding $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\mu\text{-}Me_2C.CH.CH.CO.C(Me)C(Me)\}\text{-}Mo(CO)_2(\eta\text{-}C_5H_5)]$ (II). Its reaction with allene gave $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}\eta^3,\eta^3\text{-}CMe_2CHCH(CH_2)_2\}]$ (III) and its hydrolysis and thermolysis products were found to be $[Mo_2(CO)_2(\mu\text{-}CH.CH.CMe_2)(\eta\text{-}C_5H_5)_2O]$ (IV) and $[Mo_3(CO)_4\text{-}(\mu^3\text{-}\eta^1,\eta^2,\eta^4\text{-}C.CH.CMeCH)(\eta\text{-}C_5H_5)_3]$ (V).

Reaction of 3,3-dimethylcyclopropene with $[Rh(CO)(\eta\text{-}C_5Me_5)_2]$ gave $[Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}CO.CH.CMe_2.CH)(\eta\text{-}C_5Me_5)_2]$ (VI) and with $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)]$ yielded the μ-allylidene complex $[Re_2(CO)_8(\mu\text{-}CH.CH.CMe_2)]$ (VII).

Section 3 gives experimental details of the crystal structure analyses and the synthetic work.

Tables of bond lengths and angles and atomic parameters are listed in the Appendix.

CONTENTS

Abbreviations:

Chemical

Ar	:	aryl
Bu^s	:	secondary butyl
Bu^t	:	tertiary butyl
Cp	:	cyclopentadienyl
dppe	:	bis(diphenylphosphido)ethane
dppm	:	bis(diphenylphosphido)methane
Et	:	ethyl
HFA	:	hexafluoroacetone
Me	:	methyl
Ph	:	phenyl
phen	:	phenanthroline
Pr^i	:	ispropyl
py	:	pyridine
R	:	alkyl
TCNE	:	tetracyanoethylene
THF	:	tetrahydrofuran

Theoretical

LUMO	:	lowest unoccupied molecular orbital
HOMO	:	highest occupied molecular orbital
EHMO	:	extended Hückel molecular orbital

Spectroscopic

n.m.r.	:	nuclear magnetic resonance
d	:	doublet
s	:	singlet

t	:	triplet
i.r.	:	infra red
s	:	strong

Crystallographic

e.s.d. or σ	:	estimated standard deviation
F_c	:	calculated structure factor
F_o	:	observed structure factor
I	:	intensity
μ	:	mass absorption coefficient

Section 1.1

The Chemistry of the π-Donor Acetylene Complex $[Mo(HC_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$

Introduction

π-Donation by Acetylenes

The bonding of acetylenes to transition metals can in many cases be approximated by the classical Dewar-Chatt-Duncanson model for olefins.[1,2] This involves donation from the π-orbital of the alkene to an empty hybrid orbital on the metal of σ-symmetry, and back donation from a filled metal π-orbital to the π^* level of the olefin, Figure 1.1.

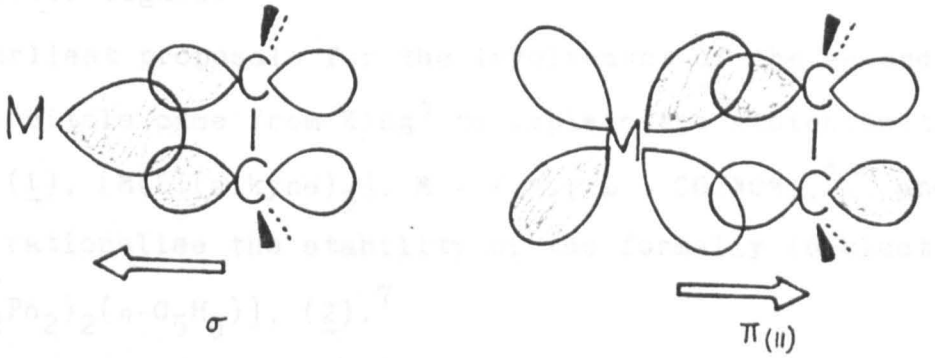


Figure 1.1. Model for Olefin Bonding to Transition Metals

Acetylenes, however, may also utilise their other set of π-orbitals, which are orthogonal to the plane containing the atoms. These $\pi_\perp$ and $\pi^*_\perp$ levels may interact with out-of-plane metal orbitals of π and δ bonding symmetry, respectively, Figure 1.2.

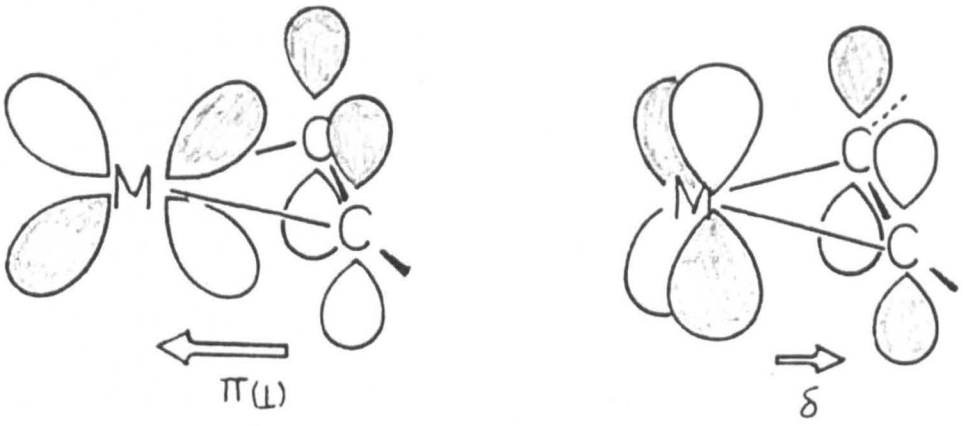
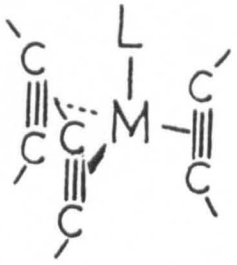


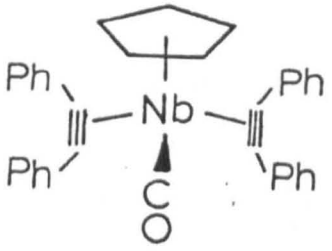
Figure 1.2 Out-of-Plane Metal Alkyne Bonding

Considerable evidence now exists that the $\pi_{\perp}$ interaction, which constitutes π-donation to the metal from the out-of-plane π-orbital of the acetylene is important to the stability of certain metal-alkyne complexes, namely those for which the metal cannot acheive an 18-electron configuration if the alkyne functions solely as a two electron donor ligand.

The earliest proposals for the involvement of the second set of alkyne π-orbitals came from King[3] to explain the stoichiometry of the complexes (1), $[M(L)(alkyne)_3]$, M = W,Mo; L = CO,NCMe,[4-6] and Nesmeyanov et al. to rationalise the stability of the formally 16 electron complex $[Nb(CO)(C_2Ph_2)_2(\eta\text{-}C_5H_5)]$, (2).[7]



(1)

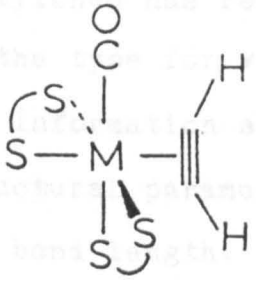
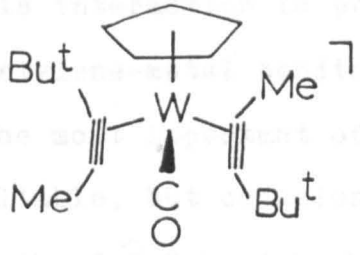
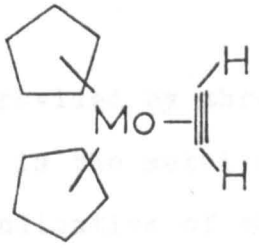


(2)

The considerable physical and theoretical evidence for acetylene $\pi_\perp$ -donation comes mainly from three sources; i) n.m.r. spectroscopy, ii) x-ray crystallography and iii) molecular orbital calculations. It is also noteworthy that many of the acetylene complexes for which $\pi_\perp$ -donation is thought to be important have either no known or only highly unstable olefinic analogues. The resistance of formally 16 electron metal-alkyne species to nucleophilic attack and ligand addition may also be understood in the light of $\pi_\perp$-donation by the alkyne.

i) N.m.r. Chemical Shifts

An empirical correlation between the number of electrons (N), formally donated per alkyne ligand (compatible with an inert gas configuration at the metal centre) and the ^{13}C n.m.r. chemical shift of the bound alkyne carbon nuclei was discovered by Templeton and Ward for a series of 10 mononuclear alkyne complexes of Mo and W.[8]

N	4	3	2
			
	(3)	(4)	(5)
	206.6 ppm (M = W)	152 ppm (av)	117.7 ppm

S^S = S_2CNH_2

For complexes such as (3) in which four electrons are formally required by the metal from the acetylene to attain an 18 electron count, the chemical shifts fall approximately in the range from 180-210 ppm, whereas in (5), in which the alkyne is constrained to be a two electron donor, the chemical shift is 117.7 ppm.[9] The only reasonable explanation for this extraordinary ^{13}C shift variation is that there is $\pi_\perp$-donation in (3). This is supported by the intermediate shifts observed for compounds such as (4)[10] in which the acetylenes may be described as 3 electron donors on the basis that the metal requires six electrons from two acetylenes. Marked chemical shift changes have also been observed in ^1H n.m.r. spectra of complexes possessing terminal acetylenes. The shift for the acetylene protons in $[Mo(CO)(C_2H_2)\{S_2P(Pr^i)_2\}_2]$ is at 12.33 ppm compared with that for $[Mo(C_2H_2)(\eta\text{-}C_5H_5)_2]$ at 7.68 ppm.[11]

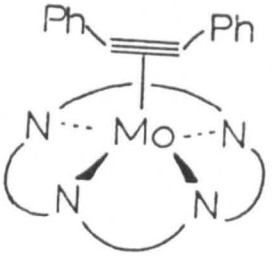
ii) Structural evidence

A considerable number of transition metal acetylene complexes have now been structurally characterised. The current interest in $\pi_\perp$-donation by acetylenes has resulted in a large proportion of these compounds being of the type for which this interaction is proposed.

Information about acetylene-metal bonding is provided by three structural parameters. The most important of these is the metal-alkyne M-C bond length. Less reliable, but occasionally indicative of the degree of $\pi_\perp$-donation is the C-$\widehat{C}$-C bend-back angle at the alkyne carbon and the alkyne C≡C bond length.

The structural differences between two and four electron donor acetylene ligands have been best illustrated by the following examples. Weiss et al. have carried out structure determinations on the pair of

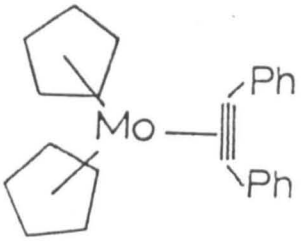
molybdenum complexes (6) and (7).[12] Compound (6) is a tetraphenylporphyrin Mo complex possessing a '4 electron' donor diphenylacetylene at the apical site of a square pyramidal coordination sphere. Compound (7) is the diphenylacetylene adduct of molybdenocene in which the alkyne is constrained to be a two electron donor.



(6)

Mo-C = 1.983,1.965(4)Å

C≡C = 1.324(5)Å



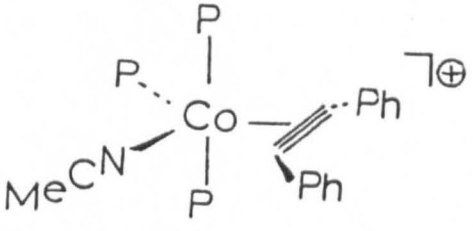
(7)

Mo-C = 2.143,2.144(6)Å

C≡C = 1.269(7)Å

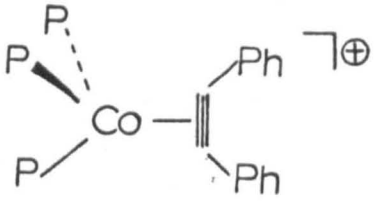
The geometry of the metal-alkyne unit differs substantially between the two species. The Mo-C bonds are much shorter in (6) than (7), whereas the C≡C bond is significantly longer in (6), this being the expected result of $\pi_{\perp}$-donation.

An even more convincing example is provided by Dartiguenave and coworkers in the structural characterisation of a pair of cationic cobalt-diphenylacetylene complexes, (8) and (9).[13]



(8)

P = PMe_3



(9)

Compound (8) may be converted to (9) by dissociative loss of an acetonitrile ligand, with the result that the alkyne switches from being formally a 2 electron to a 4 electron donor. This change is compatible with the geometric changes found for acetylene coordination in the two compounds. The Co-C bond lengths average 1.979(5)Å in (8) and 1.852(5)Å in (9). The C=C bond lengths are identical within their limits of error, however.

Table 1.1 provides a list of structural parameters for some selected transition metal complexes.[14] The general features are as shown in the above examples. Acetylene $\pi_{\perp}$-donation results in a shortening of the metal-carbon bond, together usually with associated C=C bond lengthening. The C-$\hat{C}$-C bond angles are also given where available. This parameter is found to decrease with increase in donation.

iii) Theoretical evidence

Although King had described a bonding model for the $[ML(RC{\equiv}CR')_3]$ system in 1965, detailed theoretical investigations on mononuclear alkyne complexes have appeared only recently.[15-18]

Templeton et al. demonstrated the importance of ligand π-donation in a variety of 'electron deficient' complexes, including alkyne species.[15] They have carried out EHMO calculations on the compound types $[M(CO)(C_2R_2)(S_2CNR'_2)_2]$, $[M(CO)(C_2R_2)(R')(\eta\text{-}C_5H_5)]$, $[M(O)(C_2R_2)(S_2CNR'_2)_2]$, $[M(C_2R_2)(S_2CNR'_2)_2]$, $[M(CO)_2(OR)_2(py)_2]$ and $[M(CO)_2(S_2CNR_2)_2]$, which possess formally 16 electron coordinatively unsaturated d^4 Mo(II) or W(II) metal centres. These compounds do not display the electrophilic behaviour or reactivity pattern normally expected of such compounds, despite the fact that seven coordination is

TABLE 1.1

Structural parameters for selected Transition Metal Acetylene Complexes

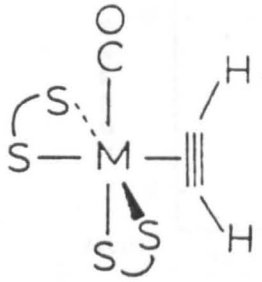
Compound	C≡C	C≡C—C	M—C	Ref.
$[Co(NCMe)(C_2Ph_2)(PMe_3)_3]^+$	1.267(7)	147.9(5)	1.979(5) (av)	13
$[Co(C_2Ph_2)(PMe_3)_3][BF_4]$	1.265(7)	143.6(5) 137.5(5)	1.851(5) (av)	13
$[Fe(C_2Ph_2)\{P(OMe)_3\}_3]$	1.332(10)			14a
$[Ni(C_2Ph_2)(CNBu^t)_2]$	1.283(14)	148.6(12)	1.899(19)	14b
$[Pt(C_2Ph_2)(PPh_3)_3]$	1.32(9)	140(5)	2.03(6)	14c
$[Pt(C_2Ph_2)_2]$	1.280(6)	153(1)	2.025(5)	14d
$[Pt_2(C_2Ph_2)_2(PMe_3)_2]$	1.26(5)	153	2.01(3)	14d
$[Ti(CO)(C_2Ph_2)(\eta\text{-}C_5H_5)_2]$	1.285(10)	142.3(7)	2.107(7) 2.230(7)	14e
$[Nb(CO)(C_2Ph_2)(C_4Ph_4)(\eta\text{-}C_5H_5)]$	1.26(3)	142.(4)	2.22(2)	14f
$[Ta(NC_5H_5)(C_2Ph_2)Cl_4][HNC_5H_5]$	1.325(12)	139.7(8)	2.068(8)	14g

exceedingly common for Mo(II) carbonyl derivatives.[19]

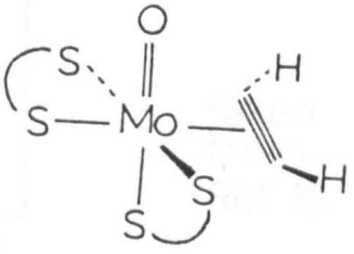
The inertness of these compounds to ligand addition processes is attributed to the destabilisation of the metal-based LUMO. In all of the above examples this may be achieved if there are filled π-donor orbitals on the ligands (eg C_2R_2, OR, SR or O) which are of the same symmetry as the LUMO. These would then combine in a bonding and anti-bonding sense; the stabilised bonding combination being filled and residing mostly on the ligand, the destabilised anti-bonding one becoming the LUMO of the complex and still localised primarily on the metal.

The amount of alkyne $\pi_\perp$-donation will then depend on whether other π-donor ligands are coordinated to the metal and thus competing with it in giving π^* character to the LUMO. The ligand composition may also govern the preferred orientation of the bound alkyne.

These points are well illustrated by compounds (3) and (10).



(3)
M=Mo



(10)

The calculations of Templeton et al.[15] clearly show distinct orientational preferences for the alkyne ligand in both complexes. However in the carbonyl species (3) the 'parallel' orientation is preferred whereas in the oxo complex (10) the alkyne lies perpendicular to the metal-oxygen vector. Figures 1.3 to 1.5 show the energy diagrams of the frontier orbitals of the compounds (3) and (10) and their

dependence on the alkyne rotation angle α = 0, 90°.

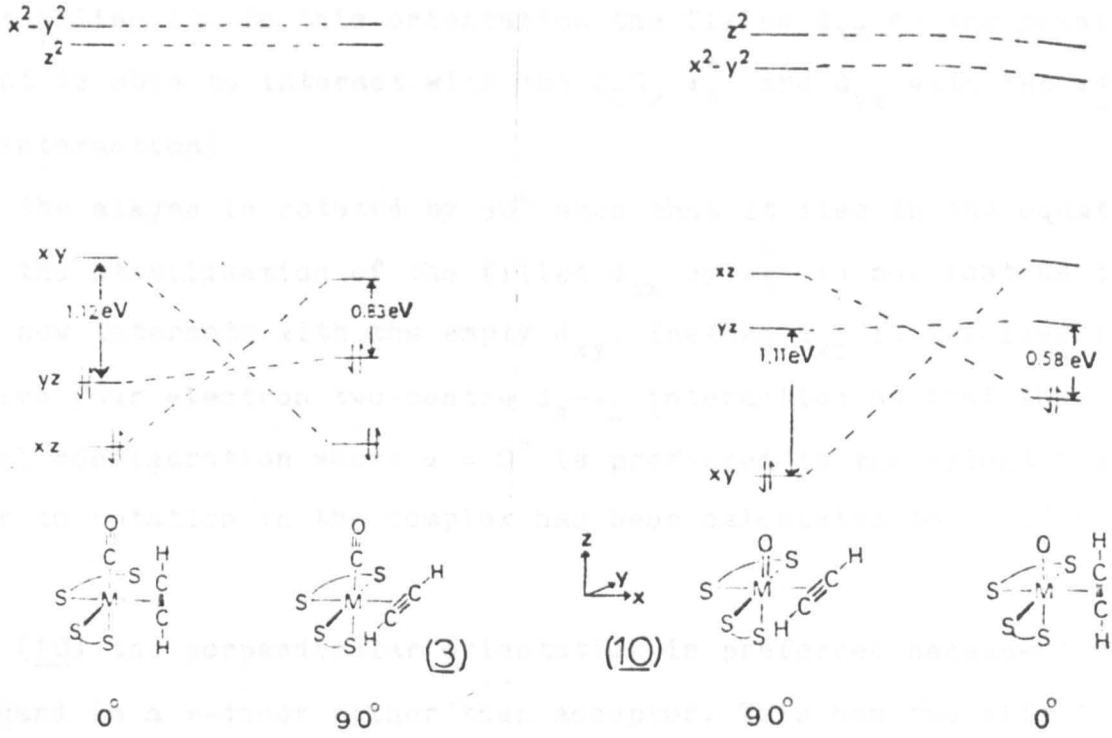
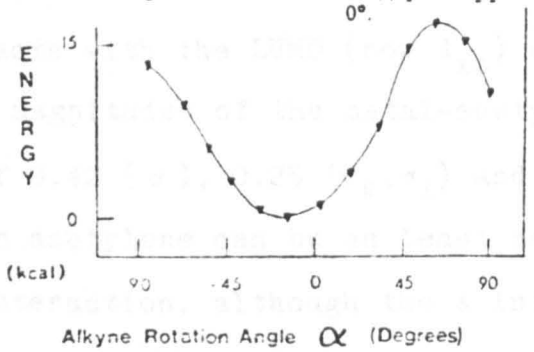


Figure 1.3 Relative frontier orbital energies for $Mo(CO)(HC{\equiv}C\text{-}H)(S_2CNH_2)_2$ as a function of the alkyne rotation angle α at 0 and 90°.

Figure 1.4 Relative frontier orbital energies for $Mo(O)(HC{\equiv}CH)(S_2CNMe_2)_2$ as a function of the alkyne rotation angle α at 90 and 0°.



taken from Ref 15.

Figure 1.5 Relative calculated total energy vs. the alkyne rotation angle α for $Mo(CO)(HC{\equiv}CH)(\pi\text{-}C_3H_5)(CH_3)$.

In (3) the π-acceptor capability of the carbonyl ligand stabilises the d_{xz} and d_{yz} metal orbitals. Addition of the acetylene along the +x axis of the $[Mo(S_2CNH_2)_2(CO)]$ fragment allows formation of the σ-bond by donation from the filled acetylene $\pi_{\parallel}$ orbital to the empty metal $d_{(x^2-y^2)}$. The extent of this interaction is independent of the rotational orientation of the C_2H_2 unit as it is of σ-symmetry.

Approach of the acetylene parallel to the M-CO vector is preferred

because the $\pi_{\perp}$ donor orbital interacts with d_{xy}, the metal based LUMO, to destabilise it. In this orientation the filled d_{xz} on the metal fragment is able to interact with the C_2H_2 $\pi^*_{\parallel}$ and d_{yz} with the $\pi^*_{\perp}$ (i.e. the δ interaction).

If the alkyne is rotated by 90° such that it lies in the equatorial plane, the stabilisation of the filled d_{xz} by $\pi^*_{\parallel}$ is now lost as the latter now interacts with the empty d_{xy}. Instead d_{xz} is involved in a repulsive four electron two-centre $d_{\pi}-\pi_{\perp}$ interaction so that the parallel configuration where $\alpha = 0°$ is preferred to the extent that the barrier to rotation in the complex has been calculated to be 10.5 kcal mol^{-1}.

In (10) the perpendicular orientation is preferred because the axial oxo ligand is a π-donor rather than acceptor. This has the effect of reordering the orbital energies of the metal fragment so that the alkyne $\pi_{\perp}$ orbital interacts with the LUMO (now d_{xz}) when $\alpha = 90°$.

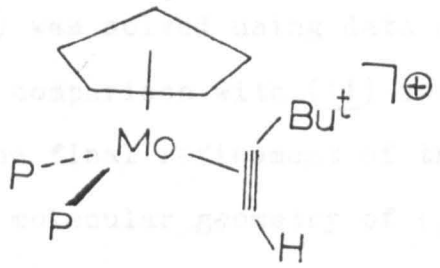
The relative magnitudes of the metal-acetylene σ, $\pi_{\parallel}$, $\pi_{\perp}$ and δ overlap values of 0.42 (σ), 0.25 ($\pi_{\parallel}$, $\pi_{\perp}$) and 0.04 (δ) show that $\pi_{\perp}$ -donation from an acetylene can be as least as strong as the π-back-bonding interaction, although the δ interaction would appear to be negligible.

In this Chapter the chemistry of a molybdenum(II) $\pi_{\perp}$-donor acetylene complex $[Mo(HC_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$, (I) will be discussed.

Synthesis of $[Mo(HC_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$

As part of a long term program in these laboratories investigating the reactivity of various coordinated ligands the complexes $[Mo(RC\equiv CR')\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ were prepared.[20]

The simplest synthetic route to these species involves oxidation of the dimer $[Mo(CO)_3(\eta-C_5H_5)]_2$ by $[AgBF_4]$ in the presence of two equivalents of the appropriate acetylene to yield the yellow compounds $[Mo(RC\equiv CR')_2(CO)(\eta-C_5H_5)][BF_4]$ followed by treatment of these with two equivalents of trimethylphosphite. Although this approach is not equally successful for all alkynes, it allows ready formation of (I), $[Mo(HC\equiv CBu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ when the acetylene used is $HC\equiv CBu^t$.[20]



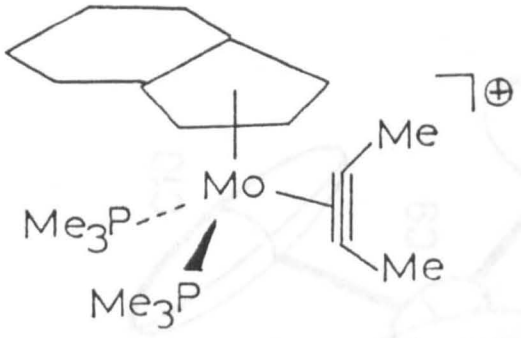
(I)

Structure Determination of $[Mo(HC\equiv CBu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$

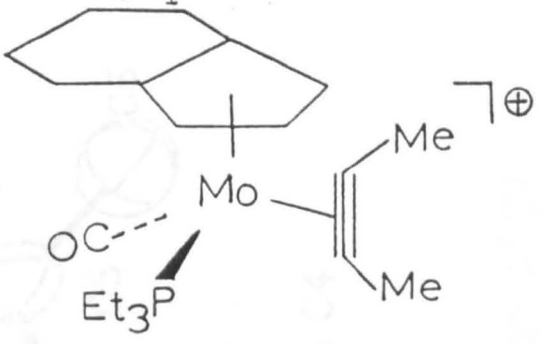
Crystals of (I) suitable for x-ray diffraction were grown as purple needles over several days by layering hexane (50ml) over a 0.1M methylene chloride solution of (I) (10ml) and allowing slow diffusion of the layers at 0°c.

The structure was of interest in that (I) falls into the class of alkyne complex for which $\pi_\perp$ -donation may be proposed. That the alkyne might be a four electron donor was indicated by the large downfield shift of the acetylenic proton, the n.m.r. signal for which was a

triplet at 11.71 ppm ($^{3}J_{P-H}$ = 15.5 Hz) and the alkyne contact carbon atoms at 201.7 ppm. Further, structural characterisations had already been carried out on the related 2-butyne complexes $[Mo(MeC{\equiv}CMe)(PMe_3)_2(\eta^5\text{-}C_9H_7)][BF_4]$, (11), and $[Mo(CO)(MeC{\equiv}CMe)(PEt_3)(\eta^5\text{-}C_9H_7)][BF_4]$ (12).[21] The short Mo-C(alkyne) contacts of 2.013(8) and 2.046(4)Å found for these respectively were indicative of strong $\pi_\perp$-donation by the alkyne.



(11)



(12)

The structure of (I) was solved using data collected at room temperature which aided comparison with (11) and (12) which were similarly determined. The final refinement of the structure had a residual R = 0.051. The molecular geometry of (I) is shown in Figures 1.6 and 1.7, these being a projection onto the plane of the cyclopentadienyl ring and a view perpendicular to this illustrating the alignment of the acetylene C≡C bond with one of the Mo-P vectors.

Compound (I) consists of discrete $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ cations and tetrafluoroborate anions between which no unusually short contacts are found.

The Mo-C(alkyne) bond lengths in (I) are 2.006(7) and 2.014(7)Å which are typical for $\pi_\perp$-donor acetylene Mo(II) complexes, as may be seen by comparison with other such structures, Table 1.2.[22] In particular these lengths are very similar to those found in the bis(trimethylphosphine) complex (11).

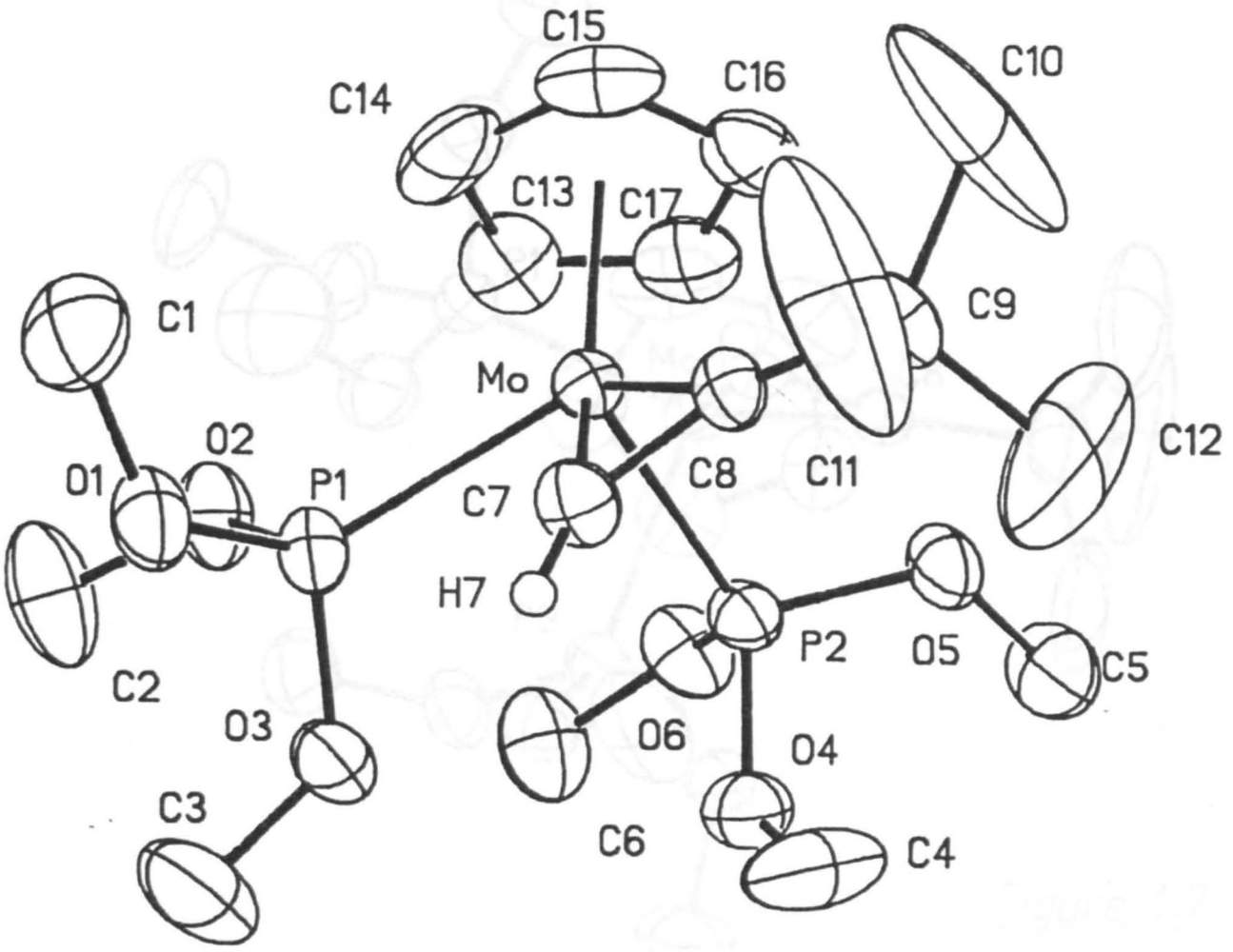


Figure 1.6 *Cation of (I)*

40% Ellipsoids

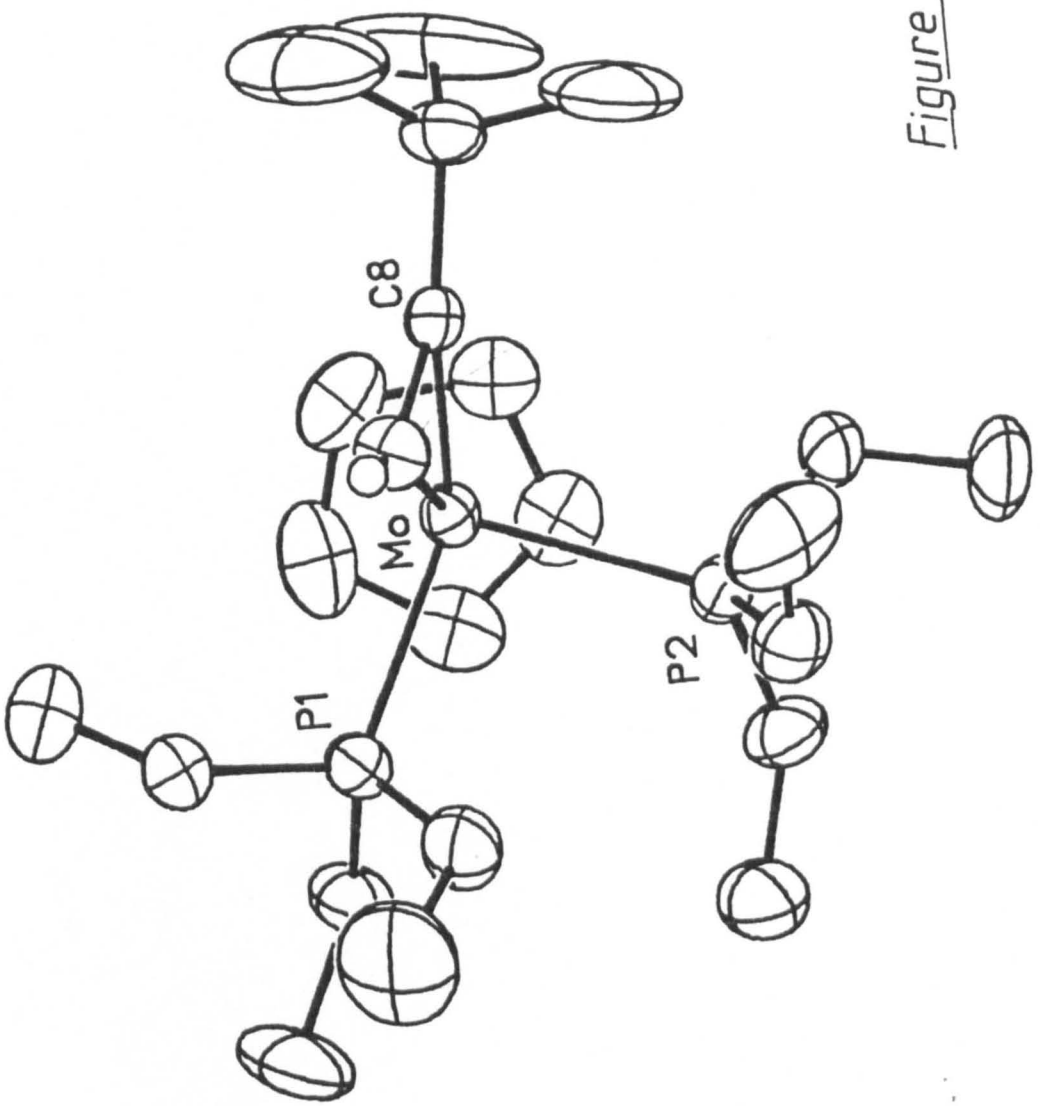


Figure 1.7

TABLE 1.2

Structural Parameters for some Molybdenum Acetylene Complexes

Ref.	Compound	Mo-C	C≡C	C-$\widehat{C}$-C
this work	(I)[Mo(HC≡CBu^t)$_2${P(OMe)$_3$}$_2$ (η-C_5H_5)][BF_4]	2.006(7) 2.014(7)	1.307(10)	137.2(7)
20	(11)[Mo(MeC≡CMe)(PMe$_3$)$_2$ (η-C_9H_7)][BF_4]	2.013(8)	1.311(11)	136.3(9)
20	(12)[Mo(CO)(MeC≡CMe)(PEt$_3$) (η-C_9H_7)][BF_4]	2.046(4)	1.291(7)	140.7(5)
12	[Mo(porphyrin)(PhC≡CPh)]	1.983(4) 1.965(4)	1.324(5)	136.4(4) 145.4(4)
18	[Mo(S_2CNEt)$_2$(CO)(PhC≡CPh)]	2.026 2.042	1.313(4)	140.3(3)
18	[Mo(η^2-S(Bu^t)$_2$S)(CNBu^t)$_2$(HC≡CH)]	2.04(2) 2.05(2)	1.28(2)	-
18	[Mo(η^2-S(Bu^t)$_2$S)(CNBu^t)$_2$ (PhC≡CPh)]	2.05(1) 2.06(1)	1.28(2)	139(1) 140(1)
21	[Mo(CO)(SC_6F_5)(CF_3C≡CCF_3) (η-C_5H_5)]	2.034(5)	1.298(6)	137.2(5)
	'3-Electron' Alkyne Complexes			
22a	[Mo(CO)(MeC≡CMe)$_2$(η-C_5H_5)][BF_4]	2.100(4)	1.272(6)	146.4(4)
22a	[Mo(NCMe)(MeC≡CMe)$_2$(η-C_5H_5)][BF_4]	2.064(4)	1.273(6)	145.4(4)
135	[Mo(PhC≡CPh)(PPh_3)(CO)(η-C_5H_5)]	2.03(1) 2.04(1)	1.29(2)	141(1) 135(1)
	'2-Electron' Alkyne Complexes			
12	(7)[Mo(PhC≡CPh)(η-C_5H_5)$_2$]	2.143(6) 2.144(6)	1.269(7)	
22b	[Mo(CF_3C≡CCF_3)(η-C_5H_4Me)$_2$]	2.128(7) 2.129(7)	1.280(10)	137.8(7) 138.8(7)

The acetylene bond C(7)-C(8) of 1.307(10)Å is longer than that found in (7) of 1.269(7)Å[12] and is consistent with extensive $\pi_{\perp}$-donation from the alkyne.

The bend-back angle C(7)-C(8)-C(9) is 137.2(7)°, which falls in the range found for four electron donor alkyne complexes and is intermediate between the average bend-back angles of the 2-butyne ligand in (11) and (12) of 136.3(9)° and 140.7(5)° respectively.

Accurate location of the acetylenic hydrogen atom H(7) could not be expected with room temperature x-ray data, though the position assigned to this on the basis of a high residual electron density peak ($0.8eÅ^{-3}$) in one of the final Fourier maps and refined without positional constraints does give a reasonable value for the C(8)-C(7)-H(7) bend-back angle of 134(4)° and which lies 0.09Å out of the [Mo-C(7)-C(8)] plane.

It is interesting to note the lack of distinct asymmetry in the Mo-C(alkyne) bond lengths in (I), C(7) which bears the hydrogen substituent being slightly closer to Mo than C(8), though the difference is only of the order of the e.s.d. of the bond length. A major discrepancy between the two bonds might have helped to account for the regiospecificity of the reaction of (I) with anionic nucleophiles such as lithium-copperalkyls and aryls. Hoffmann has argued that asymmetry in the coordination of a π hydrocarbon ligand may affect the site of attack.[23] In the case of (I), though, a different argument must be proposed.

The preferred orientation of an acetylene ligand when bonded to a $[ML_2(\eta\text{-}C_5H_5)]$ fragment has also been investigated by Hoffmann and coworkers.[24,25] A skew orientation was found to be more stable than

either an upright one or parallel one (with respect to the plane of the cyclopentadienyl ring) in cases where $L \neq L'$. The acetylene C≡C bond tends to align itself with the bond from the metal to the best π-acid ligand, such that they are coplanar. By so doing there is optimisation of the π^* backbonding interaction. The barrier to acetylene rotation for $[Mo(CO)(PH_3)(C_2H_2)(\eta\text{-}C_5H_5)]^+$ was calculated to be 30 kcal mol^{-1}, with the preferred conformation with the alkyne coplanar with the Mo-CO bond, i.e. twisted away from the 'parallel' conformation by about 20°.

Based on this analysis, the possible optimum skew orientations of the compounds (I) and (12) are considered and shown in Figures 1.8 and 1.9. For (I) two non-degenerate pairs of skew orientations would be expected due to the asymmetry of the alkyne and the fact that L = L'.

In the case of (I) only one set of signals is observed in the n.m.r. spectra for the trimethylphosphite ligands. This would indicate the presence of only one set of conformers or rapid interchange between the pairs (A) and (B) on the n.m.r. time scale.

The solid state structure of (I) reveals only cations of the form B. The dihedral angle between the plane [C(13)-C(14)-C(15)-C(16)-C(17)] and [Mo-C(7)-C(8)] is 114.5°. The conformation (A) is presumably less stable because of steric interactions that would result between the bulky ^{t}butyl substituent of the acetylene and the trimethylphosphite ligands. In accord with theoretical prediction (12) exists in the solid state as form (D), this preference being electronic rather than steric in origin.[25]

Returning to the n.m.r. of (I), a fluxional process is presumably in operation to equivalence the $[P(OMe)_3]$ groups. Interconversion of one (B) conformer to its mirror image could occur by a 'windscreen wiper' motion of the acetylene.

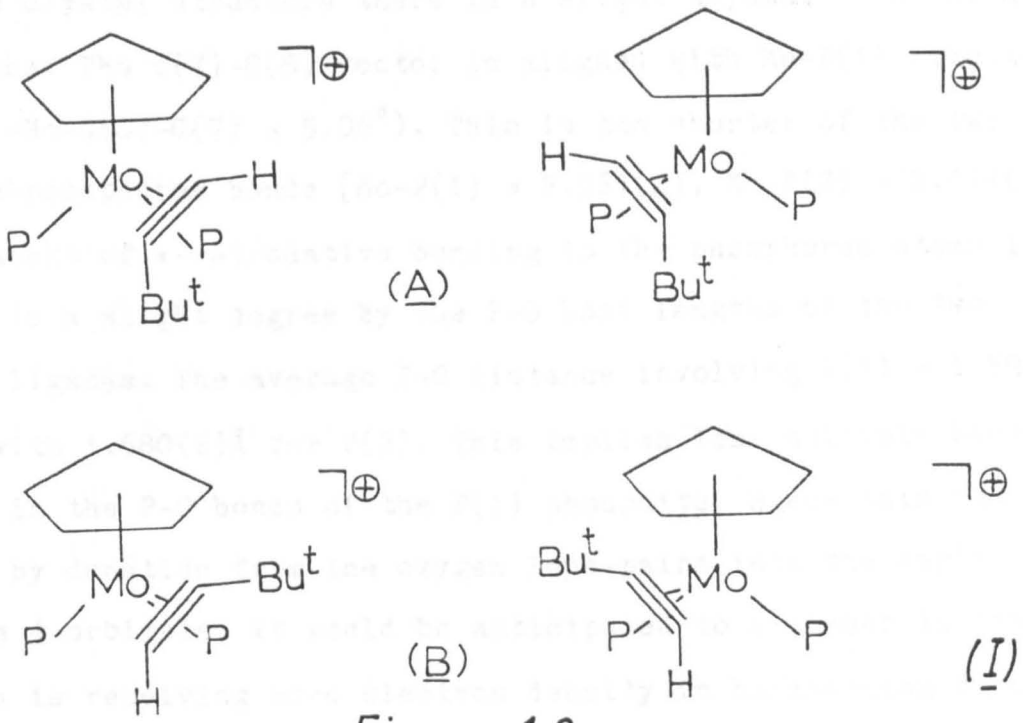


Figure 1.8

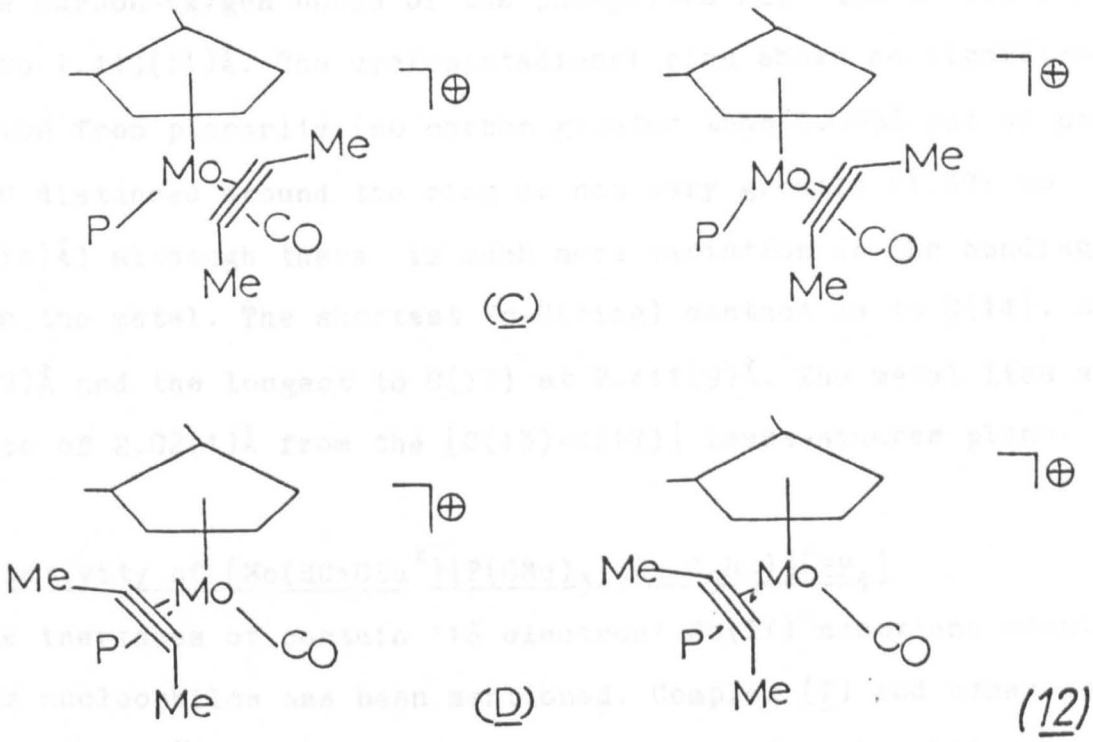


Figure 1.9

In the crystal structure there is a slight asymmetry in the Mo-P bond lengths. The C(7)-C(8) vector is aligned with Mo-P(1) (the torsion angle P(1)-Mo-C(8)-C(7) = 5.06°). This is the shorter of the two molybdenum-phosphorus bonds [Mo-P(1) = 2.367(2), Mo-P(2) = 2.414(2)Å] .

The amount of π-retrodative bonding to the phosphorus atoms is reflected to a slight degree by the P-O bond lengths of the two phosphite ligands. The average P-O distance involving P(1) = 1.596(6)Å compared with 1.580(6)Å for P(2). This implies less multiple bond character in the P-O bonds of the P(1) phosphite. Since this character is caused by donation from the oxygen lone-pairs into the empty phosphorus d orbitals, it would be anticipated to a lesser degree for P(1) which is receiving more electron density in backbonding from the metal than P(2).

The carbon-oxygen bonds of the phosphites all fall in the range 1.412 to 1.449(11)Å. The cyclopentadienyl ring shows no significant deviation from planarity (no carbon greater than 0.008Å out of plane). The C-C distances around the ring do not vary greatly (1.371 to 1.410(14)Å) although there is much more variation in the bonding of the ring to the metal. The shortest Mo-C(ring) contact is to C(14), at 2.276(9)Å and the longest to C(17) at 2.411(9)Å. The metal lies at a distance of 2.02(1)Å from the [C(13)-C(17)] least-squares plane.

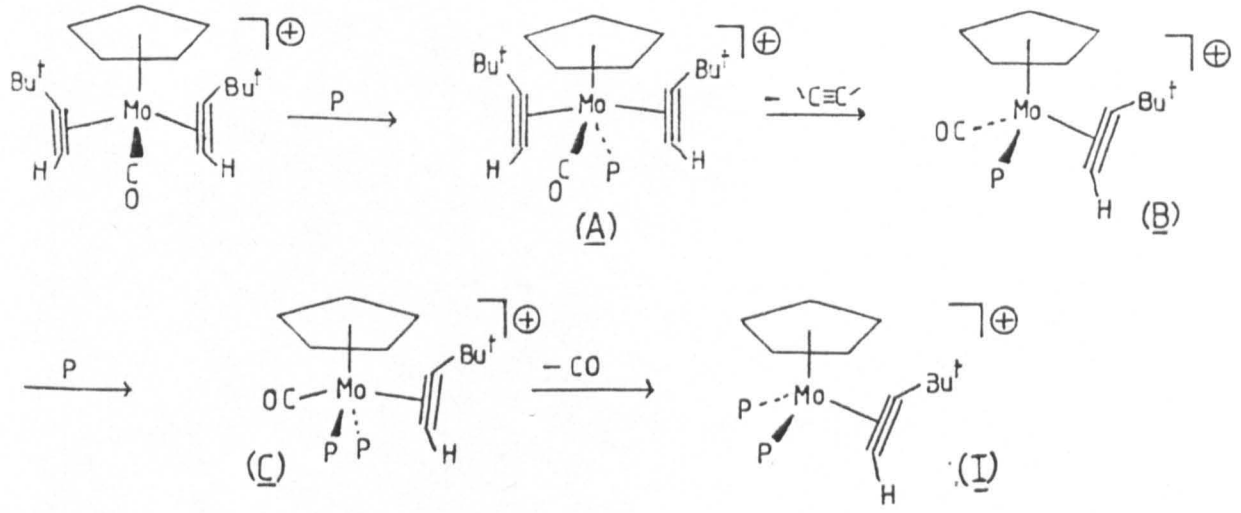
Reactivity of $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$

The inertness of certain '16 electron' Mo(II) acetylene complexes towards nucleophiles has been mentioned. Complex (I) and other acetylene complexes of its type react with a wide range of nucleophiles, especially anionic ones, e.g. H^-, SR^-, OR^-, Ar^- and R^-.[26-34]

Like the species $[Mo(S_2CNR_2)_2(HC{\equiv}CH)(CO)]$ they do not add two electron donor ligands to form stable 1:1 adducts, in which the alkyne would then be a two electron ligand itself.

The possibility of that the acetylene may switch its bonding mode from a four electron donor to a two electron donor and back again, can be used to rationalise the substitution reactions of this type of compound via an associative process.

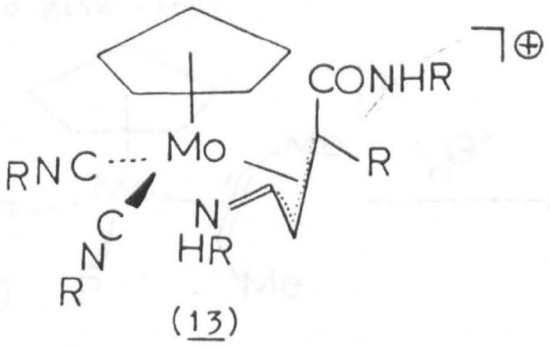
In this way the formation of (I) itself may be explained; initial addition of $[P(OMe)_3]$ to the $[Mo(CO)(HC{\equiv}CBu^t)_2(\eta\text{-}C_5H_5)]$ cation could result in the formation of a transient species (A) (Scheme 1.1). Loss of an acetylene ligand from this and exchange of the carbonyl for a second phosphite to give (I) could be facilitated by the same process. In the case of $[PMe_3]$ and other phosphines the reaction would not proceed as far as carbonyl substitution yielding complexes of the type (12).[26] This is readily understood in terms of the greater basicity of these ligands stabilising the cation sufficiently by monosubstitution.



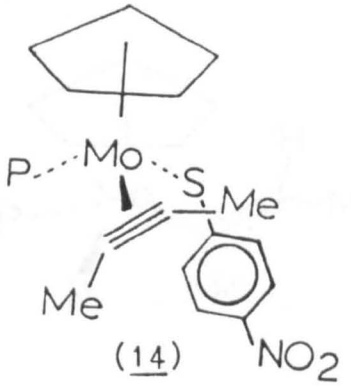
Scheme 1.1

There is precedent for coordinated ligands to show variable electron donation to a single metal centre. For example the nitrosyl ligand may be considered as either a 1 or a 3 electron donor depending on whether it is bent or linear.[35,36] Interconversion of the two forms was postulated by Collman to account for catalytic activity of certain metal-nitrosyls.[37]

Reactions of two electron donors with (I) does occur. There is for example, a rapid colour change from purple to yellow/brown when an excess of $CNBu^t$ is added to a THF solution of (I) at room temperature.[27] The only product isolated was (13) which showed extensive incorporation of isocyanide had occurred, together with hydroysis.



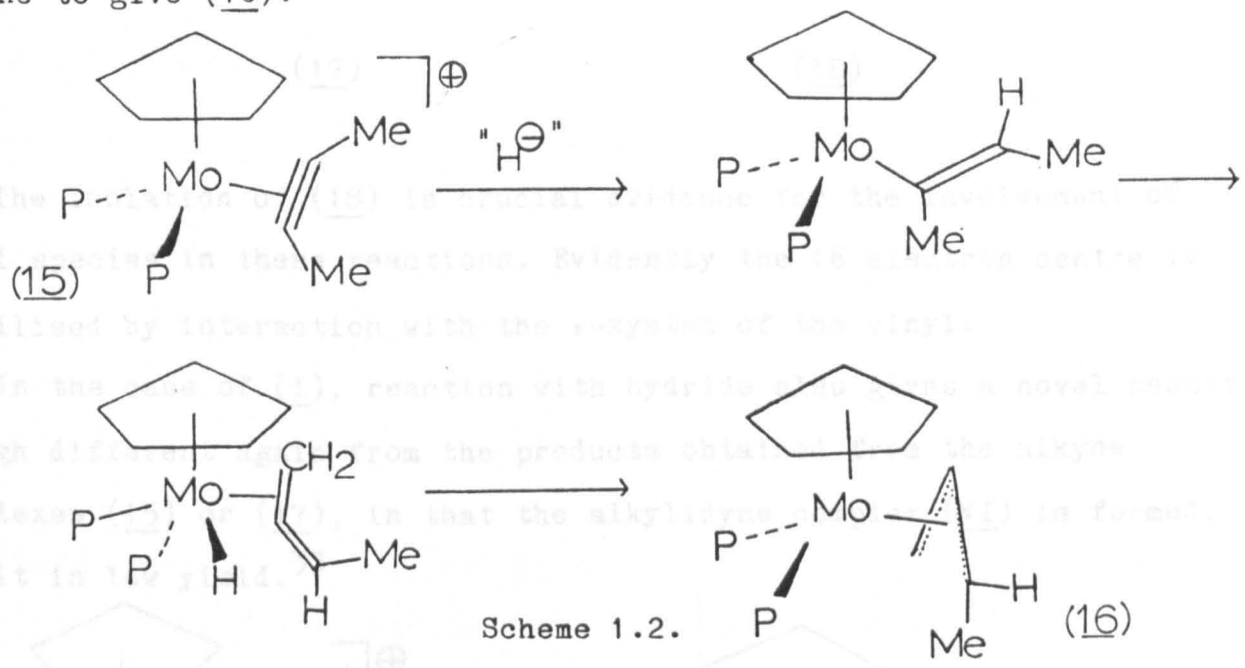
(13)



(14)

Reactions of (I) and its analogues with anionic sulphur nucleophiles resulted in the substitution of one of the phosphite ligands by the mercaptide group yielding neutral compounds such as (14).[28] The crystal structure of (14) reveals the expected orientation of the alkyne; skew and in plane with the Mo-P rather than the Mo-S vector. The substitution may again be occurring via the associative mechanism shown in Scheme 1.1. Similar results have been obtained with alkoxide[29] and arylcarbanions[30] although for the latter there are other competing pathways.

The reactions of the $[Mo(RC{\equiv}CR')\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ cations with hydride have been extensively studied in these laboratories and the results found to vary with the alkyne substituents. The 2-butyne complex $[Mo(MeC{\equiv}CMe)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (15) reacts with hydride (as either $[NaBH_4]$ or $[KBH(Bu^s)_3]$) to yield the η^3-allyl complex (16).[31] The mechanism proposed for formation of (16) is given in Scheme 1.2. It involves nucleophilic attack on the alkyne to form a 16-electron σ-vinyl intermediate, which would bear a methyl substituent on the α-carbon atom. It is then postulated that β-hydrogen abstraction from this methyl would then occur forming a hydrido(allene) complex. The metal bound hydride would then be transfered to the cental carbon of the coordinated allene to give (16).

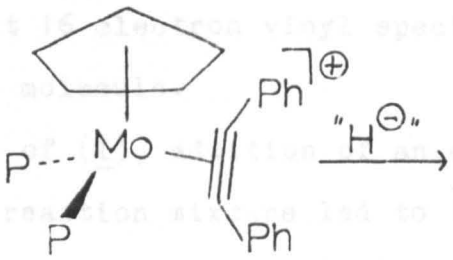


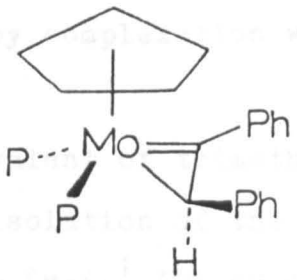
Scheme 1.2.

Precedent for this type of rearrangement comes from the observation that the iridium(I)vinyl complex $[Ir(\sigma\text{-}(E)\text{-}CMe{=}CHMe)(CO)(PPh_3)_2]$ isomerises at 90°c to the π-allyl species $[Ir(\eta^3\text{-}syn\text{-}CH_2CHCHMe)(CO)(PPh_3)_2]$.[38]

Crucial to this mechanism is the availability of β-hydrogens on the vinyl ligand of the proposed 16 electron intermediate. Although no such intermediates have been isolated or identified spectroscopically there is now considerable evidence for their involvement in these reactions.

Treatment of (17), the diphenylacetylene analogue of (I) with hydride yields (18) which was identified as a η^2-vinyl complex by x-ray crystallography.[32]

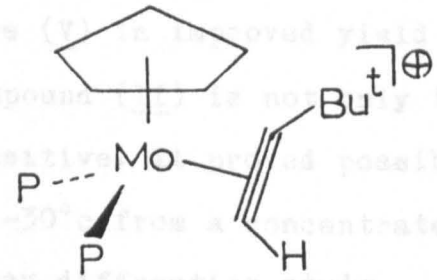


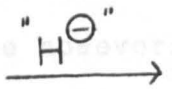


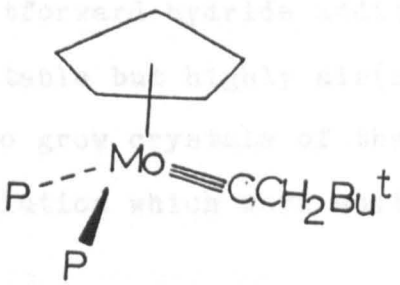
(17) (18)

The isolation of (18) is crucial evidence for the involvement of vinyl species in these reactions. Evidently the 16 electron centre is stabilised by interaction with the π-system of the vinyl.

In the case of (I), reaction with hydride also gives a novel result though different again from the products obtained from the alkyne complexes (15) or (17), in that the alkylidyne complex (VI) is formed, albeit in low yield.[33]





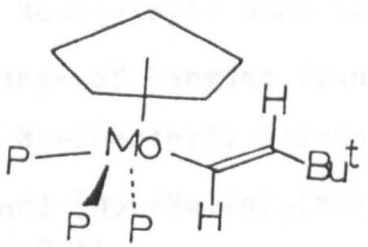


(I) (VI)

Reaction of $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with Hydride in the presence of $[P(OMe)_3]$

Formation of the η^3-allyl complex (16) from addition of hydride to (15) was found to proceed more smoothly in the presence of a further equivalent of trimethylphosphite, especially if borohydride was used as the hydride source. This might be rationalised in terms of stabilisation of the transient 16 electron vinyl species by complexation with the donor $[P(OMe)_3]$ molecule.

In the case of (I), addition of an equivalent of trimethylphosphite to the hydride reaction mixture led to the isolation of the tris(phosphite)σ-vinyl complex, (II), yellow $[Mo(\eta^1\text{-}(E)\text{-}CH{=}CHBu^t)\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]$.[34]



(II)

Thermolysis of a hexane solution of (II) (80°c,2 days) was found to give (V) in improved yield over straightforward hydride addition to (I). Compound (II) is not only thermally unstable but highly air(moisture)-sensitive. It proved possible however to grow crystals of the material at -30°c from a concentrated pentane solution which were suitable for an x-ray diffraction study.

In order to confirm the nature of (II) and investigate the stereochemistry of the σ-vinyl ligand a single crystal x-ray structure determination was carried out. This was successful, the final R factor was 0.026 and all atoms in the structure were located directly. The molecular geometry of (II) together with the atomic labelling scheme is shown in Figures 1.10 to 1.12.

Compound (II) is of the piano-stool type $[ML_4(\eta\text{-}C_5H_5)]$, which have been the subject of a theoretical study by Hoffmann et al.[39]

The vinyl ligand is σ-bound to the molybdenum and comprises one of the four piano-stool legs. It has an E-stereochemistry, so that the two vinyl hydrogens are mutually trans.

The vinyl ligand is planar at the α- and β-carbon atoms, C(10) and C(11), the bond angles about these atoms giving sums of 359.9° and 360.0°, respectively. The Mo-C(vinyl) bond length is 2.243(2)Å, which is at the short end of the range of lengths found for molybdenum-carbon σ-bonds. For example, the Mo-C(methyl) distances in $[Mo(CO)_3(Me)(\eta^5\text{-}C_{10}H_8)]_2$ and $[Mo(PMe_2Ph)_2(Me)_2(\eta\text{-}C_6H_5Me)]$ are 2.383(10)Å and 2.30(1)Å respectively.[40,41] It is closer to the values obtained for the only other structurally characterised molybdenum σ-vinyl complex $[Mo\{C(CF_3)=C(CF_3)C_5H_5\}(CF_3C\equiv CCF_3)(\eta\text{-}C_5H_5)]$ of 2.251(9)Å,[42] the η^1-iminoacyl complex $[Mo(CO)_2\{C(Me)=NPh\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ for which Mo-C(σ) = 2.272(10)Å[43] and the η^1-acyl complex $[Mo(CO)_2\{C(Me)=O\}(PPh_3)(\eta\text{-}C_5H_5)]$ Mo-C(acyl) = 2.264(14)Å.[44]

The shorter Mo-C bonds in the vinyl, iminoacyl and acyl complexes undoubtedly reflect a π contribution to the bonding between the metal and the ligand. Table 1.3 provides a more comprehensive list of structurally characterised Mo-C sigma bonds.[45]

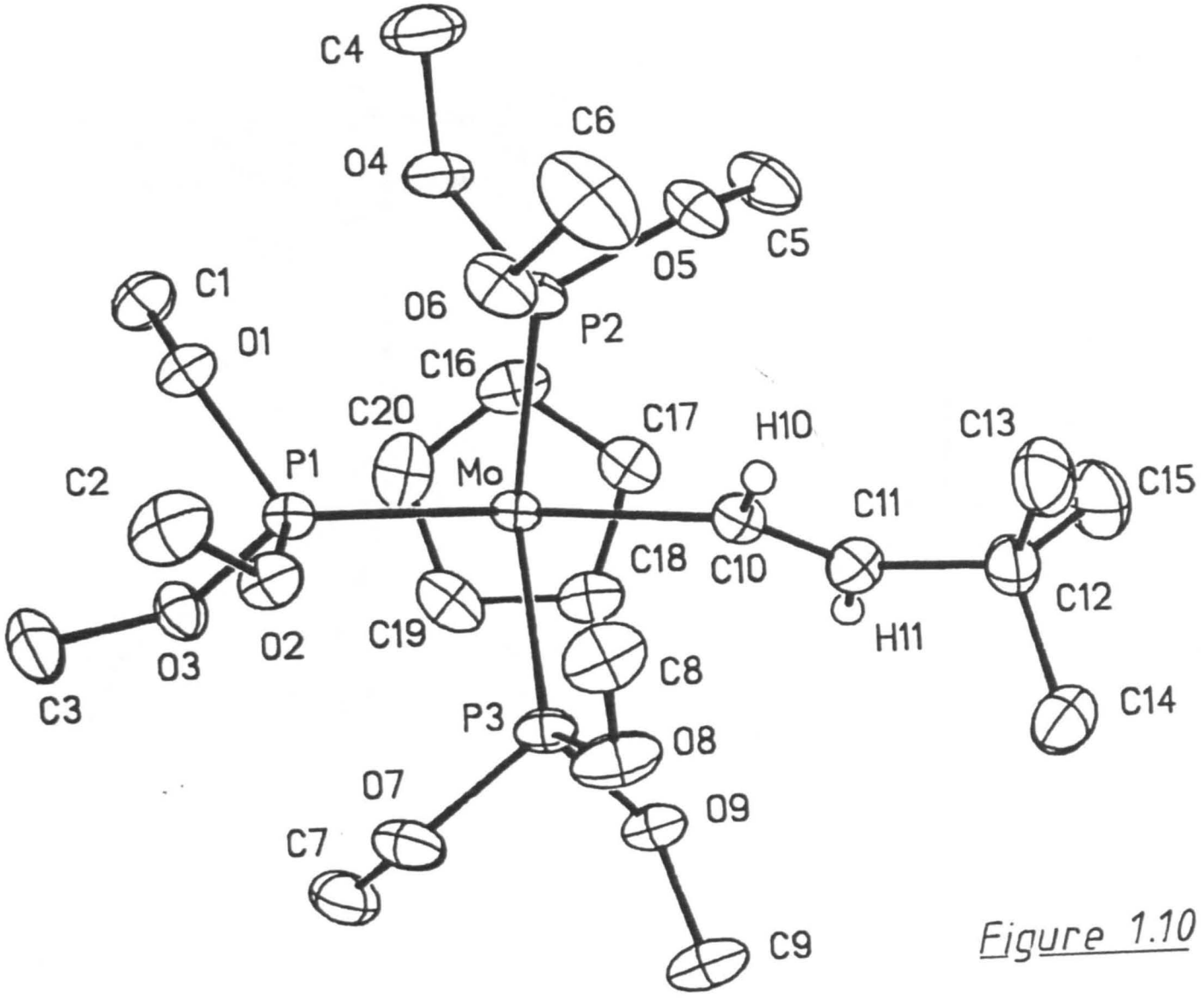

C4
C6
O4
O5
C5
C1
O6
P2
O1
C16
C20
C17
H10
C13
P1
Mo
C15
C2
C11
C18
C10
C12
O2
C19
H11
O3
C8
C3
P3
C14
O8
O7
O9
C7
C9

Figure 1.10

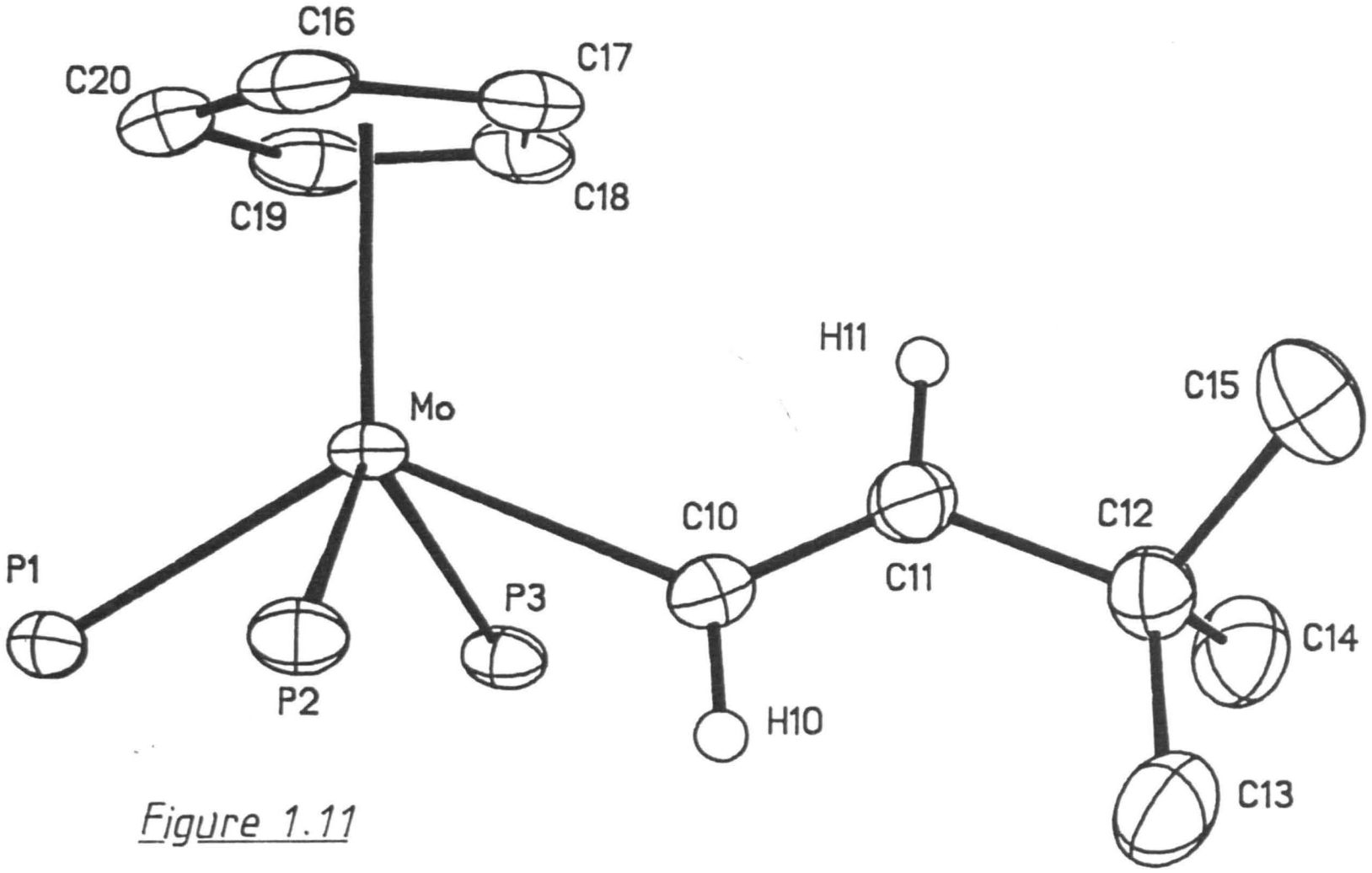


Figure 1.11

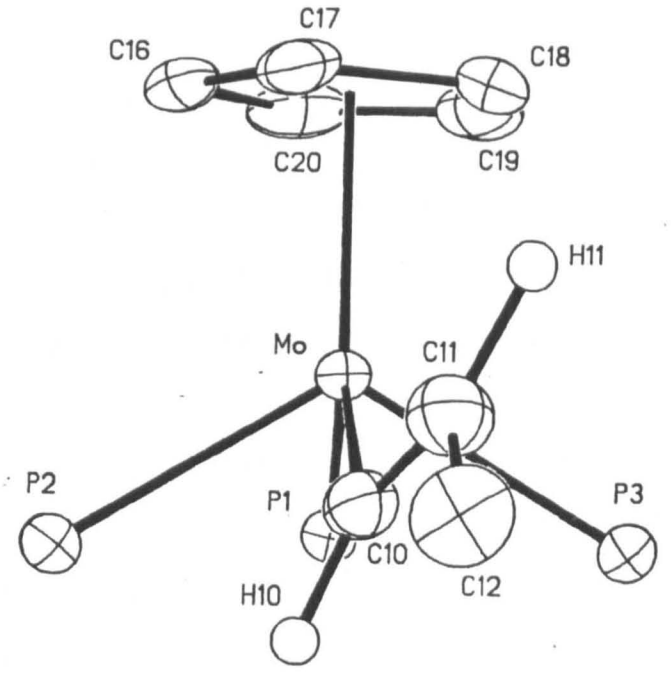


Fig. 1.12

TABLE 1.3

Selected Molybdenum-Carbon Bond Distances

Compound	Mo-C, Å	Ref.
$[Mo(CO)(\eta^4\text{-}S(Me)CO.CH.CH.CO)(\eta\text{-}C_5H_5)]$	2.071(4)	45a
$[Mo(CO)_2(\eta^2\text{-}C(OH)C(CO_2Et)=N\text{-}NH)(\eta\text{-}C_5H_5)]$	2.092(12)	45b
$[Mo(CO)_2(\eta^2\text{-}C(Me)=NPh)(\eta\text{-}C_5H_5)]$	2.106(5)	58
$[Mo(CO)_2(\eta^2\text{-}C(O).CHPh.CHMe.NHMe)(\eta\text{-}C_5H_5)]$	2.17(1)	45c
$[Mo(CO)_2(\eta^2\text{-}C(O).CH_2.CH_2.CH_2)(\eta\text{-}C_5H_5)]$	2.086(8)	56h
$[Mo(CO)_2(\eta^1\text{-}C_6F_5)(\eta\text{-}C_7H_7)]$	2.24(2)	45d
$[Mo(CF_3C{\equiv}CCF_3)\{C(CF_3)C(CF_3)(C_5H_5)\}(\eta\text{-}C_5H_5)]$	2.251(9)	42
$[Mo(CO)(\eta^1\text{-}C(O)Me)(PPh_3)(\eta\text{-}C_5H_5)]$	2.264(14)	44
$[Mo(CO)_2(\eta^1\text{-}C(Me)=NPh)P(OMe)_3(\eta\text{-}C_5H_5)]$	2.272(10)	43
$[Mo(CO)_3(\eta^1\text{-}C_3F_7)(\eta^1\text{-}C_5H_5)]$	2.288(8)	45e
$[Mo(CH_3)_2\{PMe_2Ph\}_2(\eta\text{-}C_6H_6)]$	2.30(1)	41
$[Mo(CO)_2(\eta_2\text{-}CH.CH_2.CH_2.AsMe_2)(\eta\text{-}C_5H_5)]$	2.35(1)	45f
$[Mo(CO)_3(CH_3)(\eta^5\text{-}C_{10}H_8)]_2$	2.383(10)	40
$[Mo(CO)_3(C_2H_5)(\eta\text{-}C_5H_5)]$	2.38 (2)	45h
$[Mo(CO)_3(CH_2COOH)(\eta\text{-}C_5H_5)]$	2.36(2)	45g
$[Mo(CO)_2(C(CN)_2C(CN)_2Me)PPh_3(\eta\text{-}C_5H_5)]$	2.414(4)	45i

It is interesting that inspite of the short Mo-C(10) bond in (II) there is no significant lengthening of the C(10)-C(11) vinyl 'double' bond. This is 1.336(3)Å which is close to the accepted C=C bond length of 1.34Å in ethylene.[46] Small changes in C≡O bond length have also been observed for terminal coordination of carbon monoxide and this seems to be a general finding for multiply bonded systems.

The orientation of the vinyl ligand in (II), like that of the alkyne in (I) lies neither parallel or perpendicular to the plane of the cyclopentadienyl ring; instead the plane [Mo-C(10)-C(11)-C(12)] makes an angle of 68.8° to the (η-C_5H_5) ring.

The orientational preferences of carbene and vinylidene ligands bonded to [$ML_2(\eta$-$C_5H_5)$] fragments have been analysed[24] and found to be electronically determined; the conformation for which the ligand π-acceptor orbitals lie parallel to the plane of the cyclopentadienyl group being preferred. In the case of such ligands bonding to a [$ML_3(\eta$-$C_5H_5)$] fragment the preference appears to be the same. In [Mo{C(OEt)Ph}($GePh_3$)$(CO)_2(\eta$-$C_5H_5)$] the plane of the carbene ligand is perpendicular to the C_5-ring so that the acceptor p-orbital on the ligand is in the optimal 'parallel' conformation.[47]

In the case of a vinyl ligand the electronically preferred orientation should be the same as that of the carbene. The skew conformation found in (II) is probably due to steric effects and may simply reflect a low barrier to rotation about the Mo-C bond. This would be in accord with the temperature invariant (183-293K) ^{31}P n.m.r. spectrum of (II) which is an AB_2 spin system, implying time-averaged molecular C_s symmetry in solution.[34]

The phosphorus P(1) transoid to the vinyl shows the shortest Mo-P bond (2.352(1)Å). The average Mo-P(cisoid) is 2.363(2)Å, which tends to indicate that phosphite is a better π-acceptor ligand than the vinyl ligand.

The interligand angles in the basal plane are in the usual range for $[ML_4(\eta\text{-}C_5H_5)]$ complexes[39] and show the distortions expected for the smaller bulk of the vinyl relative to the trimethylphosphites. The transoid angles are P(1)-Mo-C(10) = 127.1(1)°, P(2)-Mo-P(3) = 117.1(1)°. The cisoid angles are P(1)-Mo-P(2) = 80.6(1)°, P(1)-Mo-P(3) = 81.5(1)°, C(10)-Mo-P(2) = 74.1(1)° and C(10)-Mo-P(3) = 70.5(1)°. The bonding of the cyclopentadienyl ring to the molybdenum shows less asymmetry than found for (I), the Mo-C(ring) distances falling in the range 2.307(2)Å to 2.370(2)Å.

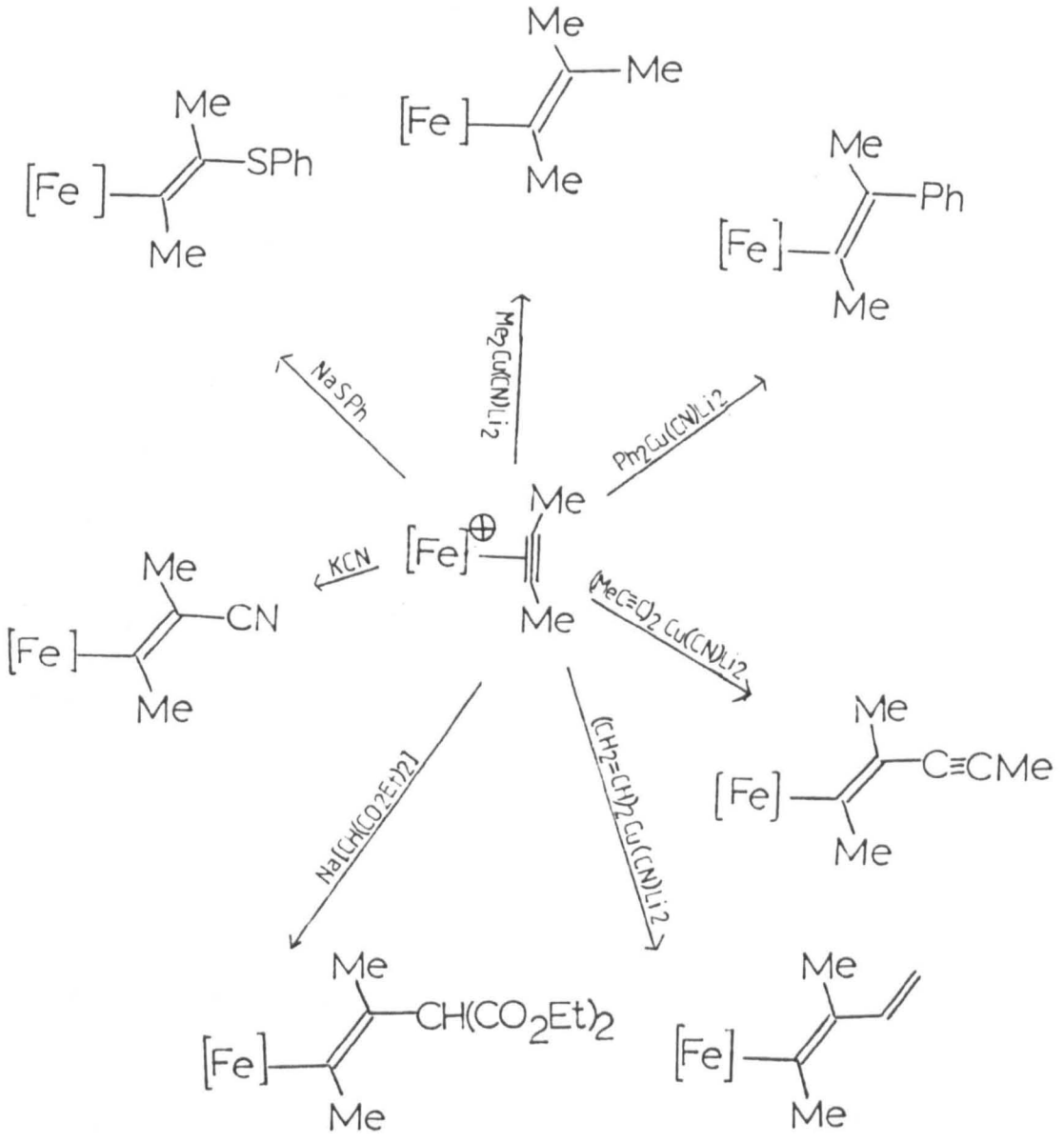
Other examples of nucleophilic attack on cationic alkyne complexes have appeared in the literature. Chisholm and Clark reported the reaction of cationic Pt(II) compounds of the type trans-[Pt(Me)L2-(alkyne)][PF6] with methanol to yield β-methoxyvinyl or methoxycarbene complexes.[48]

More closely related is the work of Reger et al.[49,50] They have reacted a variety of cationic iron compounds eg $[Fe(CO)(PPh_3)(MeC{\equiv}CMe)(\eta\text{-}C_5H_5)][BF_4]$ (19) with a range of organic nucleophiles to form 18 electron σ-vinyl products (Scheme 1.3)

Formally these should bear a close resemblance to (II), the fragments $[FeL_2(\eta\text{-}C_5H_5)]$ and $[MoL_3(\eta\text{-}C_5H_5)]$ being isolobal. It should be noted that in the iron complexes the alkyne is acting only as a 2 electron ligand.

Scheme 1.3.

Nucleophilic Additions to Cationic Iron Alkyne Complexes



Fe = CpFeCO(L) L = $P(OPh)_3$, PPh_3

Reaction of $[Mo(HCCBu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ with hydride in the presence of CO

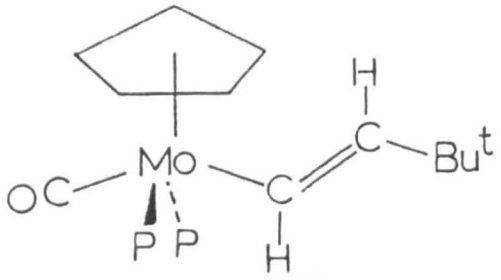
In order to synthesise the vinyl complex (III), $[Mo(CO)(\sigma-CH=CHBut)\{P(OMe)_3\}_2(\eta-C_5H_5)]$, the reaction of (I) with hydride was carried out in the presence of carbon monoxide. The target molecule was of interest in seeing whether it could rearrange to the alkylidyne complex $[Mo(CO)(CCH_2Bu^t)P(OMe)_3(\eta-C_5H_5)]$ to provide a high yield synthesis of the latter.[51]

A slow stream of CO was bubbled through a THF solution of (I) for 10 mins prior to addition of one equivalent of $[KBHBu^s_3]$ (potassium selectride) at -78°c. Passage of carbon monoxide through the reaction mixture was maintained and the vessel allowed to slowly warm to room temperature, until the reaction was deemed complete (1hr) by a colour change from deep purple to yellow-brown.

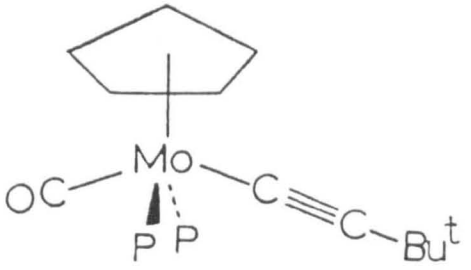
Work-up of the product mixture indicated that the reaction was not selective, several bands being collected by column chromatography on alumina.

The major fraction, eluted by a 2:1 hexane:Et_2O mixture yielded a yellow crystalline solid. The n.m.r. spectra indicated that this was a mixture of two compounds. Two sets of signals characteristic of ^{t}butyl, cyclopentadienyl and trimethylphosphite protons were observed in a ratio of 3:1 in the ^1H n.m.r. spectrum. In addition to these there were two other resonances at 6.5 and 5.6ppm which were doublets of triplets. These were assigned to the two vinyl protons of the complex (III). Each proton is coupled to the other ($^3J_{(H-H)}$ = 17Hz) and two equivalent phosphorus nuclei, presumably of two phosphite ligands cis to the vinyl. The greater $J_{(P-H)}$ coupling to the 6.5ppm resonance (18Hz rather than

1Hz) indicated that this signal was due to the proton on the α-carbon. By integration the peaks due to the vinyl protons were found to belong to the minor component of the mixture.



(III)



(IV)

The major component was identified as the acetylido complex (IV) trans-$[Mo(CO)(C{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ on the basis of its ^1H, ^{13}C n.m.r. and mass spectra. Pure (IV) obtained by repeated columning of the product mixture showed two absorptions in the region 2200-1600 cm^{-1} at 1875 and 1855cm^{-1}. These were attributable to ν-CO and ν-C≡C stretches.

Confirmation of this characterisation of (IV) came from its crystal structure determination. Crystals of (IV) were grown from hexane at -30°C. Data were collected at room temperature and the structure refined to R = 0.027. The bond lengths and angles of one of the trimethyl-phosphite ligands were affected by positional disorder of two of its methoxy groups. The molecular geometry of (IV) is illustrated in Figures 1.13-1.15.

Like (II), compound (IV) is a $[ML_4(\eta\text{-}C_5H_5)]$ complex. The crystal structure confirms the trans orientation of the two phosphite ligands. The acetylide ligand, like the carbonyl which is trans to it, is

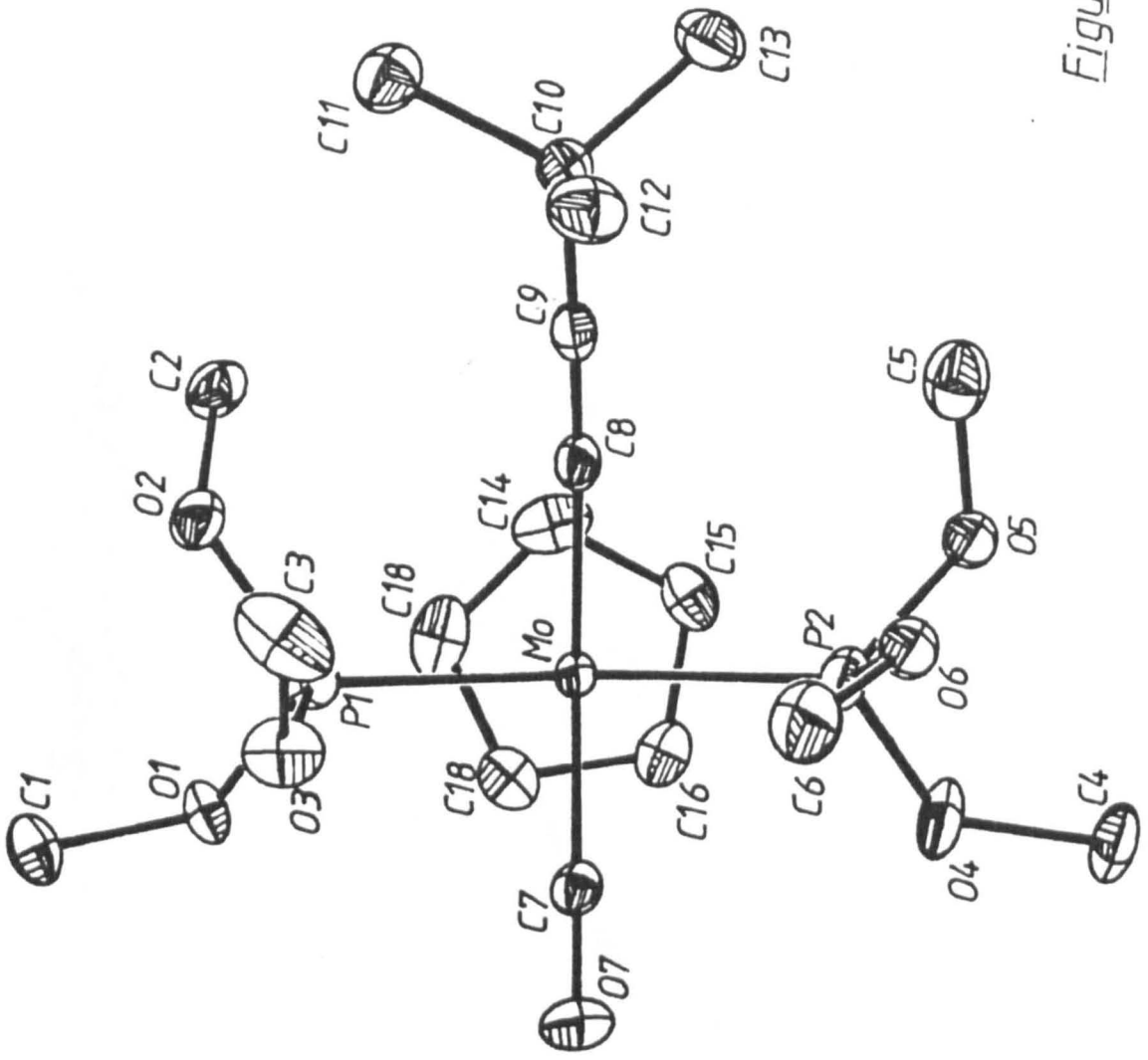

C11
C10
C13
C12
C9
C2
C8
C5
O2
C14
O5
C3
C15
C18
Mo
P2
P1
O6
C1
O1
C18
C16
C6
O3
C4
C7
O4
O7

Figure 1.13

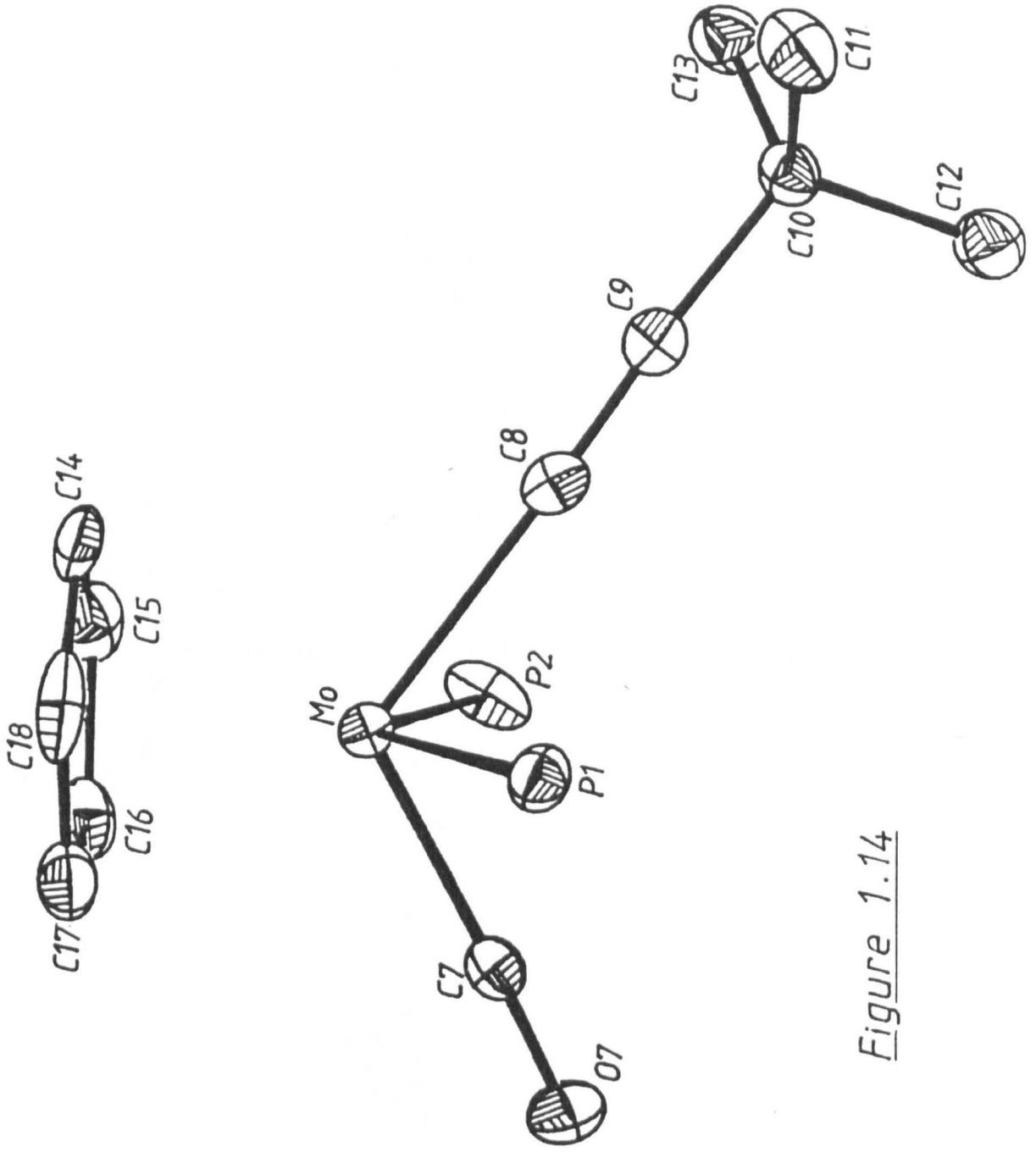


Figure 1.14

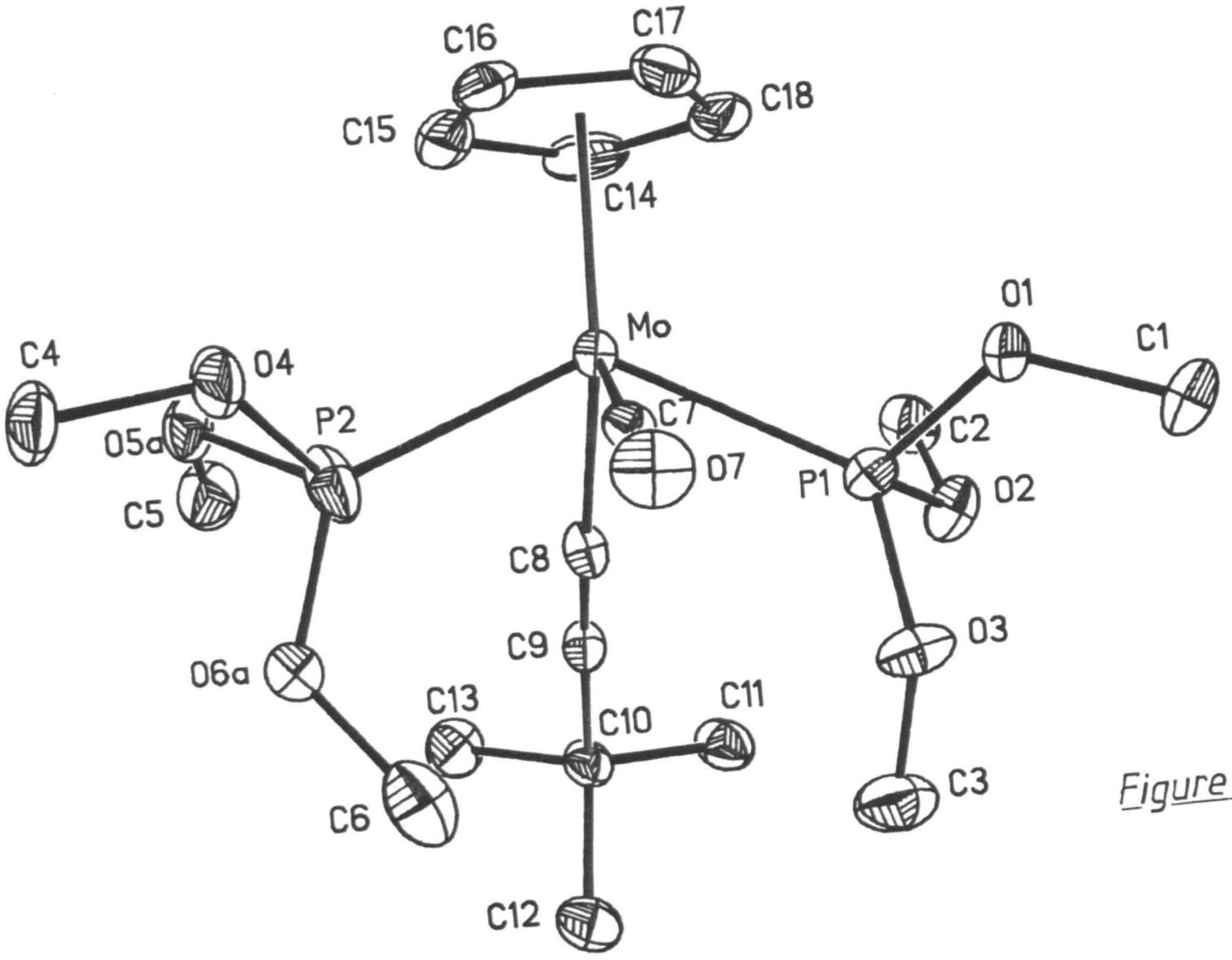

C16
C17
C18
C15
C14
Mo
O1
C1
C4
O4
P2
O5a
C5
C7
O7
C2
O2
P1
C8
C9
O3
O6a
C13
C10
C11
C6
C3
C12

Figure 1.15

approximately linear; the angle Mo-C(8)-C(9) is 176.7(5)° and the Mo-C(7)-O(7) angle 177.9(3)°.

The Mo-C(8) acetylide bond is 2.167(4)Å considerably shorter than that found for the molybdenum-carbon σ-bond in the vinyl complex (II) and other formally single Mo-C bonds, of which a comprehensive list has been given in Table 1.3.

The Mo-C bonds are found to be longest when the carbon ligand is saturated and there is no possibility of a π-type interaction with the metal. In (IV) the acetylide ligand has two sets of π^* orbitals which may interact with filled metal orbitals, compared with just one set for the vinyl ligand in (II). This, together with the slightly smaller radius expected for an sp rather than an sp^2 hybridised carbon atom, accounts for the contraction by 0.08Å of the Mo-C bond from (II) to (IV).

The same phenomenon has been found for the platinum(II) complexes $[Pt(C{\equiv}CPh)\{PEt_2Ph\}_2Cl]$ and $[Pt(CH{=}CH_2)\{PEt_2Ph\}_2Cl]$.[52] The Pt-C bond of 1.98(1)Å in the σ-acetylide complex being shorter than that of 2.03(1)Å found for the vinyl species.

Other transition metal acetylide complexes exhibit short metal-carbon contacts. For example the Fe-C(acetylide) bond length of 1.92(1)Å found for $[Fe(CO)_2(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (20),[53] is shorter than that expected (1.98-2.03Å) for Fe-C(sp) bonds.

The acetylide C(8)-C(9) bond of 1.213(5)Å in (IV) is similar in length to the C≡C bond of 1.216(8)A in $[Mn(CO)_4(C{\equiv}CPPh_3)Br]$[54] and 1.21(2)Å in (20). The C≡C triple bond in free $[C_2Ph_2]$ is 1.198(2)Å.[55]

The molybdenum-carbonyl linkage is 1.931(5)Å, which may be compared with other Mo-CO bonds in Table 1.4.[56]

TABLE 1.4

Selected Molybdenum-Carbonyl Bond Distances

Compound	Mo-CO, Å	Ref.
$[Mo(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)]$	1.951(3)	56a
$[Mo(CO)(NO)(\eta\text{-}C_5H_4R)(\eta\text{-}C_3H_5)][PF_6]$ R=neomenthyl	2.096(8)	56b
$[Mo(CO)_3(CH_3)(\eta\text{-}C_{10}H_7)]_2$	2.003(11), 1.996(12), 1.988(12)	40
$[Mo(CO)_2(Cl)\{P(OMe)_3\}_2(\eta\text{-}C_3H_5)]$	2.04(3), 1.92(3)	56c
$[Mo(CO)_3(\eta\text{-}C_6Et_6)]$	1.943(5), 1.948(5), 1.946(5)	56d
$[Mo(CO)_2(I)_3(\eta\text{-}C_5H_4Me)]$	2.045(6), 2.041(6)	56e
$[N(Bu)_4][Mo(CO)_3(\eta\text{-}C_5H_5)]$	1.921(10), 1.905(9), 1.901(8)	56f
$[Mo(PhC{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$	1.97(1)	135
$[Mo(CO)(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)][BF_4]$	2.001(4)	22a
$[Mo(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5H_5)\{MeC(NPh)\}]$	1.958(6), 1.926(5)	43
$[Mo(CO)(SC_6F_5)(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$	1.995(5)	21
$[Mo(CO)(I)(\eta\text{-}C_5H_5)\{C(NMe_2)(CMeNMe)\}]$	1.945(6)	59
$[Mo(CO)_2(Cl)(dppe)(\eta\text{-}C_3H_5)]$	1.966(13), 1.955(13)	56g
$[Mo(CO)_2(I)(\eta\text{-}C_5H_5)(\overline{COCH_2.CH_2.CH_2})]$	1.991(9), 2.007(9)	56h
$[Mo(CO)(H)(\eta\text{-}C_5H_5)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$	1.926(5), 1.923(5), 1.941(5), 1.991(5)	56i

There is no crystallographically imposed mirror symmetry in (IV), although like compounds (I) and (II) the molecule has potential C_s symmetry. As might be expected the structural parameters for the two phosphite ligands are similar; Mo-P(1) = 2.409(1)A and Mo-P(2) = 2.394(2)Å. These are longer than the corresponding distances in (II), reflecting the better π-acceptor capabilities of the ligands cis to the phosphites in (IV).

The cisoid angles about the ML_4 basal plane are more uniform than for (II), reflecting the similar steric requirement of the acetylide and carbonyl ligands; C(7)-Mo-P(1) = 76.9(1)°, C(7)-Mo-P(2) = 78.0(1)° compared to C(8)-Mo-P(1) = 74.6(1)° and C(8)-Mo-P(2) = 76.0(1)°. The transoid angles have a greater discrepancy than in (II); C(7)-Mo-C(8) = 113.4(2)° and P(1)-Mo-P(2) = 129.1(1)°.

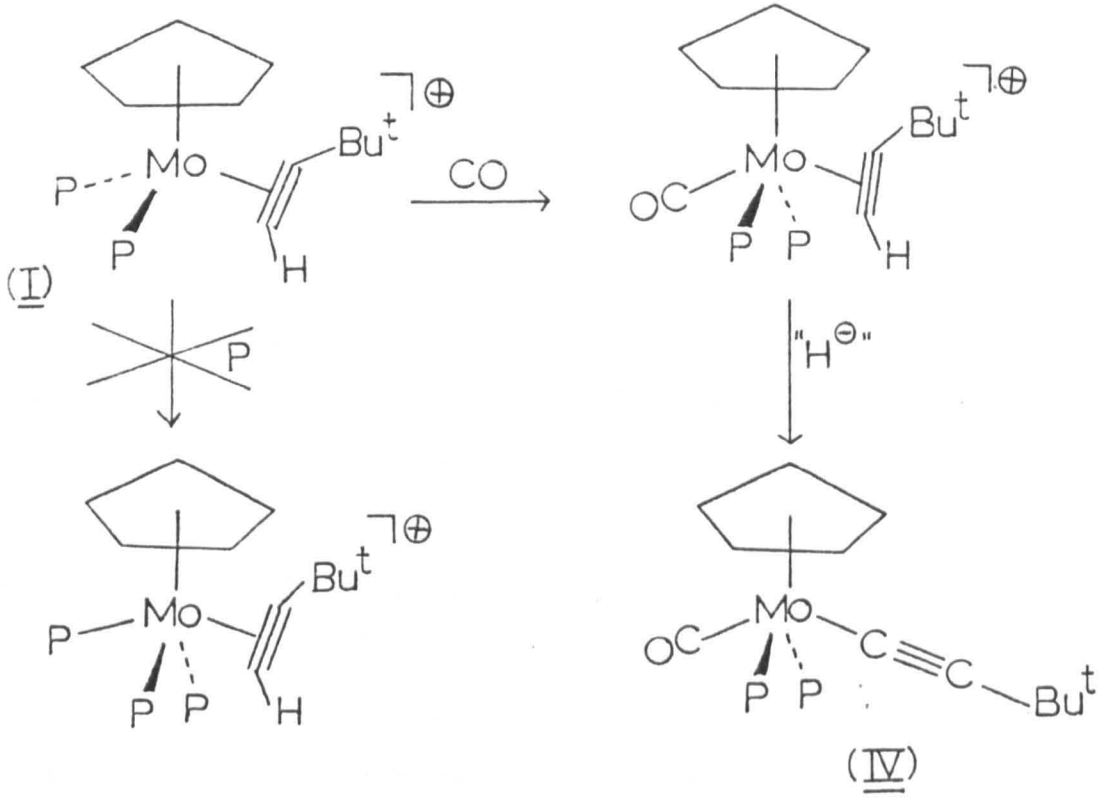
The cyclopentadienyl carbons are at the familiar range of distances from the molybdenum (2.306-2.394(6)Å).

Mechanism of the Formation of (IV)

Reaction of the acetylene complex (I) with hydride and $[P(OMe)_3]$ was found to give only one isolable product, the vinyl complex (II). Replacement of free trimethylphosphite by carbon monoxide evidently allows other reaction pathways to occur. In particular preferential formation of an σ-acetylide rather than a σ-vinyl complex must be explained.

The most plausible answer (Scheme 1.4) is that prior to attack by hydride, (I) may pre-associate with carbon monoxide (the reverse of this step having already been postulated for the formation of (I)). The acetylenic proton of this cationic complex would be expected to be

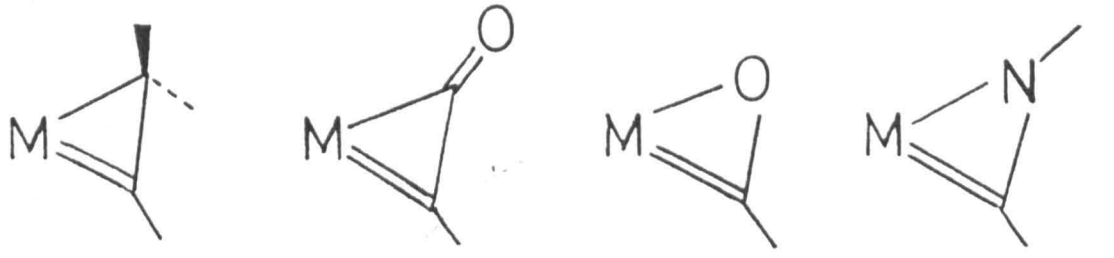
appreciably more acidic than its counterpart in (I) because of the destabilising influence of the π-acceptor carbonyl ligand. Under the basic reaction conditions deprotonation of this species might be expected, thus forming the stable σ-acetylide complex (IV). This process is in competition with vinyl formation via initial attack of hydride on (I). It is still uncertain whether this proceeds by direct attack on the alkyne ligand or at the metal centre followed by transfer of the hydride to the acetylene. Either way the effect would be to form a transient η^2-vinyl complex which would switch to η^1-coordination upon addition of free ligand (either [P(OMe)3] or [CO]). There is an obvious reason why this is the exclusive process in the trimethylphosphite reaction, which is that association of a third bulky [$P(OMe)_3$] ligand to (I) would be sterically very unfavorable if not impossible.



Scheme 1.4

Molecular Geometries of η^2-Vinyl Complexes: the structure of (V) $[\overline{Mo{=}C(Me)\text{-}CPh_2}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

Until recently the only transition metal vinyl complexes that had been characterised were those in which the vinyl ligand was sigma or η^1-bound to the metal. The possibility of an alternative bonding mode for vinyl ligands involving π or η^2-coordination was suggested by the fact that this had been observed for the related ketenyl,[99] acyl[57] and iminoacyl [58,59] functionalities (Figure 1.16) in a number of compounds.



η^2-vinyl η^2-ketenyl η^2-acyl η^2-iminoacyl

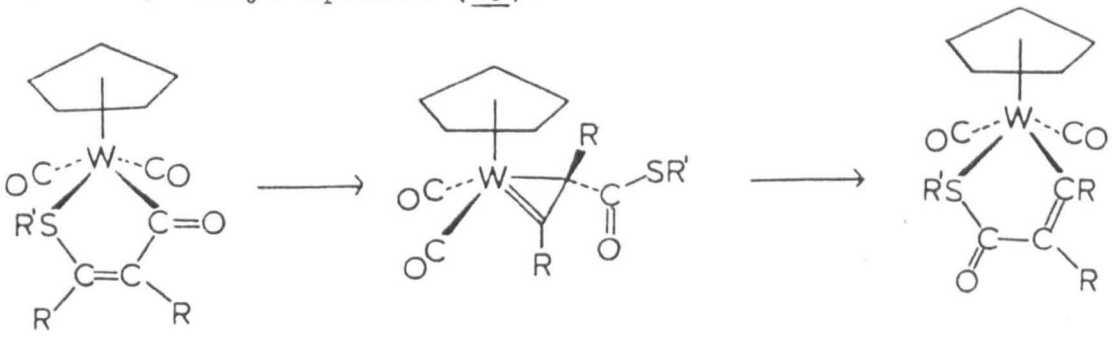
Figure 1.16 η^2-Functionalities

Synthesis of η^2-Vinyl Complexes

The addition of hydride to $[Mo(PhC{\equiv}CPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5][BF_4]$ to yield $[\overline{Mo{=}C(Ph)\text{-}CHPh}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5]$ (18) was the first report of the formation of a η^2-vinyl (or metallacyclopropene) complex.[32] Many other examples have now been synthesised in these laboratories. For example, (I) reacts with $[LiCuPh_2]$ to yield the η^2-vinyl species (21), $[\overline{Mo{=}C(Bu^t)\text{-}CHPh}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, which like (18) has been structurally identified by x-ray crystallography.[60]

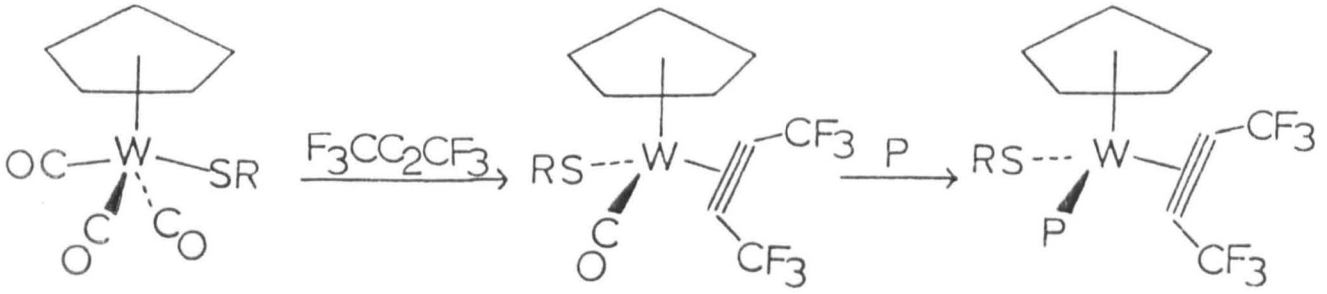
Davidson and coworkers have also reported the formation of several η^2-vinyl complexes.[61-63] Rearrangement of the tungstacycles (22) which

possess an acyl function, to the vinyl complexes (24) was found to proceed via η^2-vinyl species (23).[61]



(22) (23) (24)

The compounds (22) were formed on reaction of the thioalkyl complexes $[W(CO)_3(SR')(\eta\text{-}C_5H_5)]$ R' = alkyl, with hexafluorobut-2-yne. If R' = CF_3 or C_6F_5, the products are (25).[64] There is evidence that this process, in which two carbonyl groups are substituted for a four electron donor $[CF_3C{\equiv}CCF_3]$ ligand also involves η^2-vinyl intermediates analogous to (23).[62] Addition of phosphines to (25) yields (26) with further loss of CO. The mechanism of this substitution may involve the

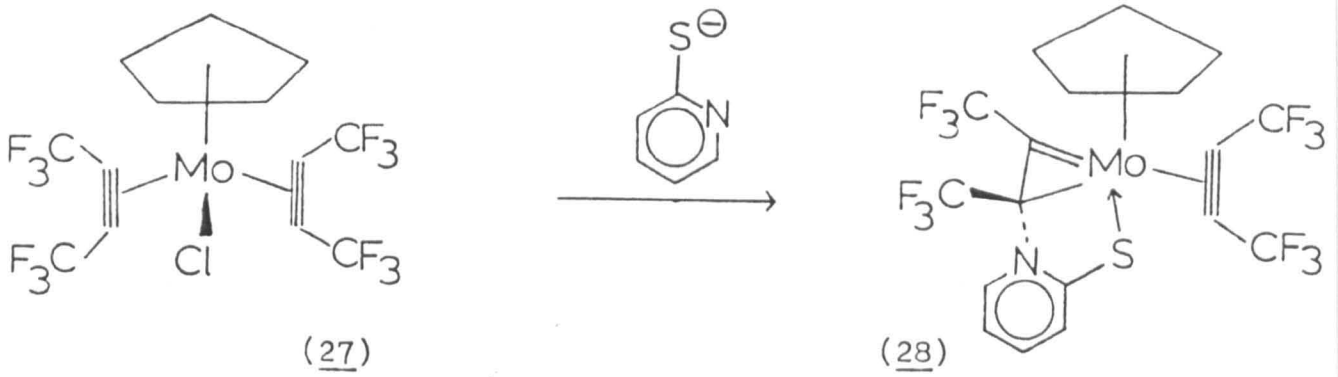


(25) (26)

2 electron/4 electron 'switch' in bonding mode for the acetylene that has been discussed previously. Davidson prefers a mechanism in which coordination of the phosphine induces migration of the SR' group onto

the alkyne to yield a η^2-vinyl, followed by expusion of CO and transfer of SR' back to the metal.[62]

Reactions of the complexes $[M(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)Cl]$ M=Mo,W with the thallium salts [Tl(LL')] proceed by nucleophilic attack of the LL'^- on the alkyne ligand to yield η^2-vinyl complexes such as (28) which was studied crystallographically.[63]



(27) (28)

Similarly addition of nucleophilic ligands such as phosphines and isocyanides to (27) apparently gives direct attack on the alkyne forming the related η^2-vinyls (29), $[M(CF_3C{\equiv}CCF_3)\{\eta^2\text{-}CF_3C\text{-}C(CF_3)L\}(\eta\text{-}C_5H_5)X]$ where X is a halide or mercapto group.[62] For these complexes, as for (28), a zwitterionic resonance form may be written, which places a negative charge on the metal and a positive one on the heteroatom bonded to the vinyl carbon.

These results strongly suggest that nucleophilic attack is occuring directly at an alkyne carbon atom rather than at the metal centre with subsequent rearrangement. It is possible that addition of hydride to complexes like (16) also proceed in this way. Unfortunately labelling studies do not distinguish between the two mechanisms so that a definite conclusion about them cannot be drawn. It should be pointed out that the alkyne carbons in Davidson's complexes (27) bear strongly electron

withdrawing substituents which may increase their susceptibility to direct nucleophilic attack.

Structural studies of η^2-Vinyl Complexes

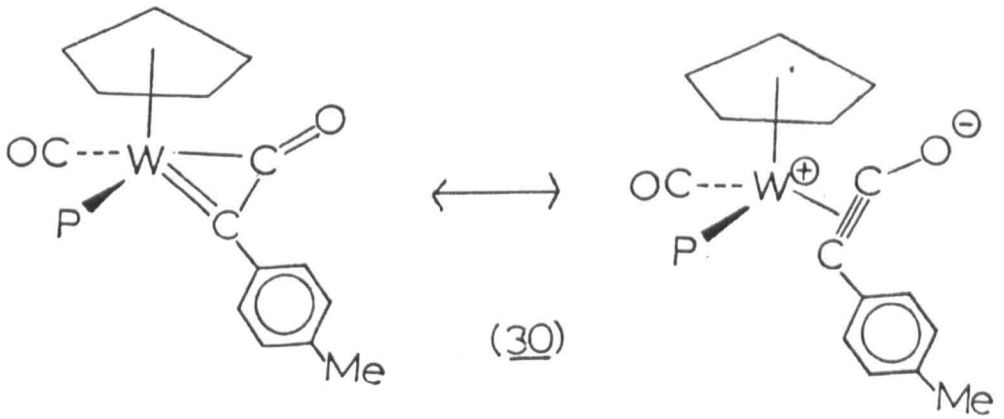
Since 1979 several structural determinations have been carried out on η^2-vinyl complexes. Table 1.5 lists the critical structural parameters derived from these studies.

The η^2-vinyls are characterised by a very short metal-carbon bond to the carbon atom (C_α) bearing one substituent. These fall in the range 1.894(8) to 1.963(4)Å for Mo and W examples given. The values correspond to tungsten and molybdenum-carbon double bonds and are somewhat shorter even than the values obtained for carbene complexes of these elements.

The bond from the metal to the vinyl 'β' carbon, that possessing two substituents, is found to vary more substantially in length. Typically, though, this lies between 2.2 and 2.3Å, indicative of a metal-carbon single bond for Mo and W.

The C_α-C_β bond of the η^2-vinyls would seem to retain considerable π-character, the bond lengths of 1.40-1.45Å being intermediate for C-C single and double bonds.

In contrast the C_α-C_β linkage for the η^2-ketenyl complex (30) is much shorter at 1.32(1)Å. This may be rationalised by a contribution from the zwitterionic canonical form to the resonance hybrid of (30).

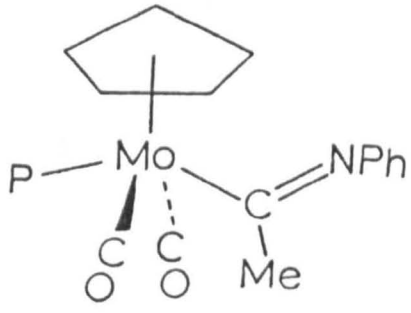


(30)

TABLE 1.5

Structural Parameters for η^2-Vinyl and related Complexes of Tungsten and Molybdenum

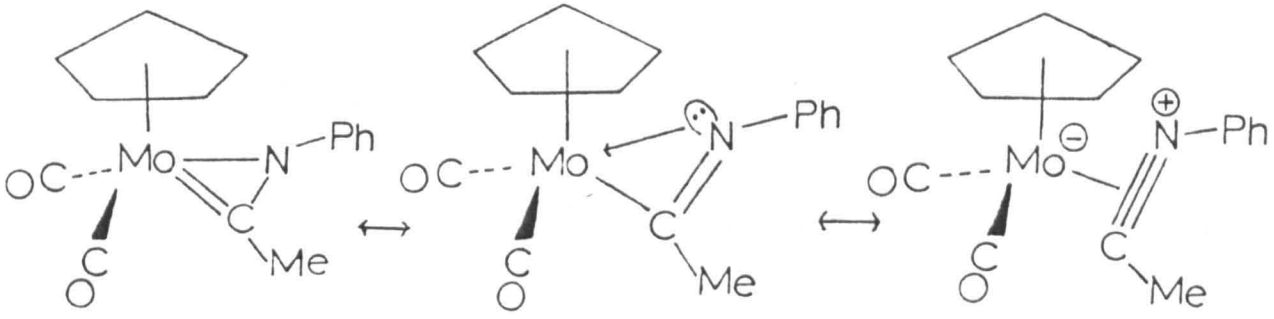
Compound	M-Cα	M-Cβ	Cα-Cβ	Ref.
η^2-Vinyl Complexes				
$[W\overline{=C(CF_3).C}(CF_3).C(O)SMe(CO)_2(\eta\text{-}C_5H_5)]$	1.96(1)	2.19(1)	1.44(1)	61
$[Mo\overline{=C(CF_3).C}(CF_3).N$  $S(\eta^2\text{-}CF_3{\equiv}CF_3)(\eta\text{-}C_5H_5)]$	1.914(4)	2.120(3)	1.390(5)	63
$[W\overline{=C(CF_3)-C}(CF_3)CNBu^t(\eta^2\text{-}CF_3{\equiv}CF_3)(Cl)(\eta\text{-}C_5H_5)]$	1.894(8)	2.304(10)	1.410(12)	64
$[W\overline{=C(CF_3).C}(CF_3).PEt_3(\eta^2\text{-}CF_3C{\equiv}CF_3)(SC_6H_4Me)(\eta\text{-}C_5H_5)]$	1.910(5)	2.330(5)	1.448(6)	64
$[Mo\overline{=C(Ph).C}HPh\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$	1.950(3)	2.300(3)	1.434(4)	32
$[Mo\overline{=C(Bu^t)}CHPh\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$	1.942(3)	2.282(3)	1.437(5)	60
$[Mo\overline{=CMe.C}Ph_2\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, (V)	1.963(4)	2.249(4)	1.463(5)	This
$[Mo\overline{=C(SiMe_3)}CH_2\{P(OMe)_3\}_2(\eta\text{-}C_9H_7)]$, (VII)	1.957(3)	2.260(4)	1.436(5)	work
η2-Ketenyls				
$[W\overline{=C(C_6H_4Me)}CO(CO)(PMe_3)(\eta\text{-}C_5H_5)]$	1.97(1)	2.07(1)	1.32(1)	99
	Cβ-O 1.30(1)			
η2-Iminoacyls				
$[Mo\overline{=C(Me).N}(Ph)(CO)_2(\eta\text{-}C_5H_5)]$	2.106(5)	Mo-N 2.143(4)		58
	C-N 1.233(6)			



(31)

This would also account for the Cβ-O bond length of 1.30(1)Å which is long for a C=O double bond.

Adams and Chodosh have observed an interesting structural phenomenon relating the η^1- and η^2-iminoacyl complexes (31) and (32) in that the C=N bond contracts on η^2-coordination. This highly unusual result was explained by the fact that the iminoacyl in (32) possesses increased 'acetylenic' character (form c). Significant contributions of forms b) and c) to the hybrid of (32) also account for the Mo-Cα bond length of 2.106(5)Å, much longer than typical of η^2-vinyls.[59]



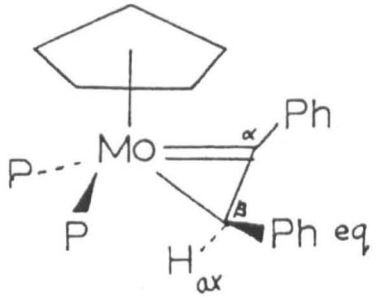
a) b) c)

(32)

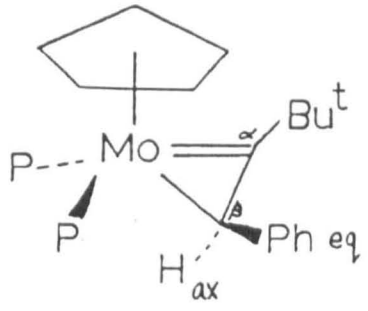
The structures of the η^2-vinyls also provide information on the stereochemistry and orientation of the vinyl ligand.

The complexes (18) and (21) differ chemically only in the substituent on the α-carbon, phenyl and ^{t}butyl respectively. The stereochemistry about the Cβ carbon atom is the same, with a phenyl group pointing away from the phosphite ligands in what shall be described as the equatorial position and a hydrogen atom in the more sterically demanding axial site. This is interesting in view of the fact that (18) is formed by attack of hydride on the $[C_2Ph_2]$ complex (16) whereas (21) is formed by attack of 'Ph^-' on (I). Thus the attacking

nucleophile is ending up in the axial position in (18) yet the equatorial one in (21).



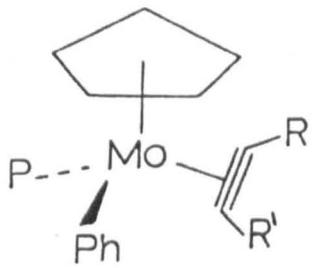
(18)



(21)

This may be explained in two ways; i) a different mechanism is operating in the two reactions or ii) a dynamic process is operating which allows the η^2-vinyl ligand to attain its prefered ground-state geometry.

The first option would mean that the site of attack by hydride is different to that by Ph^-. There is evidence that attack by Ph^- on the compounds $[Mo(RC{\equiv}CR')\{P(OMe)_3\}_2(\eta\text{-}C_5H_5][BF_4]$ to yield η^2-vinyl species does not proceed via initial attack at the metal. This comes from isolation of complexes of the type (33), which do arise from such an attack, and their resistance to η^2-vinyl conversion when treated with donor ligands.[30]



(33)

This would seem to rule out this pathway for Ph^- reactions, though it is conceivable that hydride attack may proceed in this manner.

The stereochemistry of the η^2-vinyl ligands in (18) and (21) can also be accounted for by the same mechanism if the vinyl ligand itself is able to rotate. (Figure 1.17)

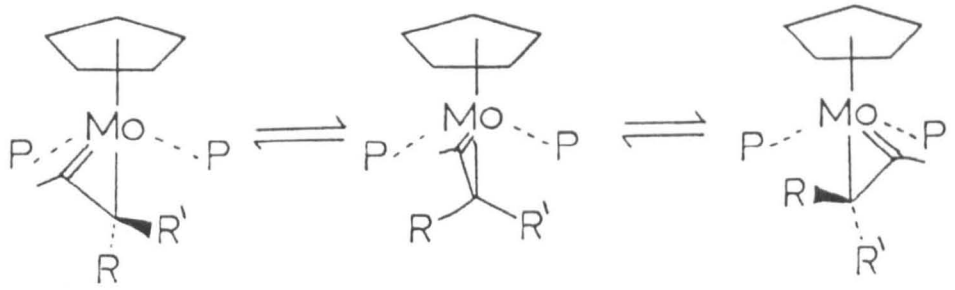


Figure 1.17 Stereochemical interconversion of a η^2-vinyl ligand

This process amounts to a polytopal rearrangement at the metal atom which traverses a 3:3:1 coordination geometry, a type discussed by Hoffmann et al. for $[CpML_4]$ complexes.[39] Similar fluxional behaviour was invoked to explain the equivalence of the carbonyl groups in the ^{13}C n.m.r. of (32).[59]

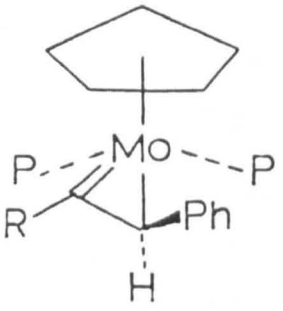
In the case of (21), the ^{31}P n.m.r. gave an AB pattern of signals at room temperature indicating inequivalence of the the phosphite groups.[66] This indeed was the case for the majority of the η^2-vinyl complexes synthesised in our laboratories.[60,66]

One exception was the compound (V), the product of the reaction of one equivalent of $[LiCuPh_2]$ to the cationic alkyne complex $[Mo(MeC{\equiv}CPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$. The spectroscopic data indicated the presence of a η^2-vinyl ligand, the α-carbon resonance was at 237ppm and the β-carbon at 36ppm in the ^{13}C n.m.r. spectrum.[66] The ^{31}P n.m.r. spectrum consisted only of a singlet and the $[P(OMe)_3]$ protons for the

two phosphite ligands were also found to be n.m.r. equivalent. This indicated that the molecule either possessed a plane of symmetry or that a dynamic process was occurring which effected a 'time-averaged' mirror plane for the molecule in solution.

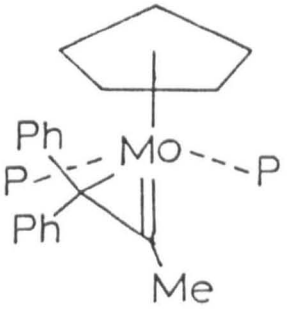
A crystal structure determination was carried out to discover whether (V) had mirror symmetry in the solid state.

The structure was solved and refined to R = 0.034 allowing the location of all non-hydrogen atoms. The x-ray results confirmed that (V) was the η^2-vinyl complex $[\overline{Mo=C(Me)-C}Ph_2\{P(OMe)_3\}_2(\eta-C_5H_5)]$, the molecular geometry of which is shown in Figures 1.18 and 1.19. No mirror was found for (V), but the orientation of the vinyl ligand was found to be quite different than that found for compounds (18) and (21). In all three complexes the coordination geometry about the metal is that of a 'four-legged' pianostool, distorted towards a capped trigonal bipyramid: i.e one of the pianostool legs sits below the plane of the other three, away from the plane of the cyclopentadienyl ring. In (18) and (21) it is the β-carbon of the η^2-vinyl ligand which occupies this pseudo-apical site, whereas in (V) it is the carbene or α-carbon.



(18) R = Ph

(21) R = Bu^t



(V)

The reason for this change is probably steric; both the substituents on the Cβ carbon of (V) are phenyl groups, one of which therefore would

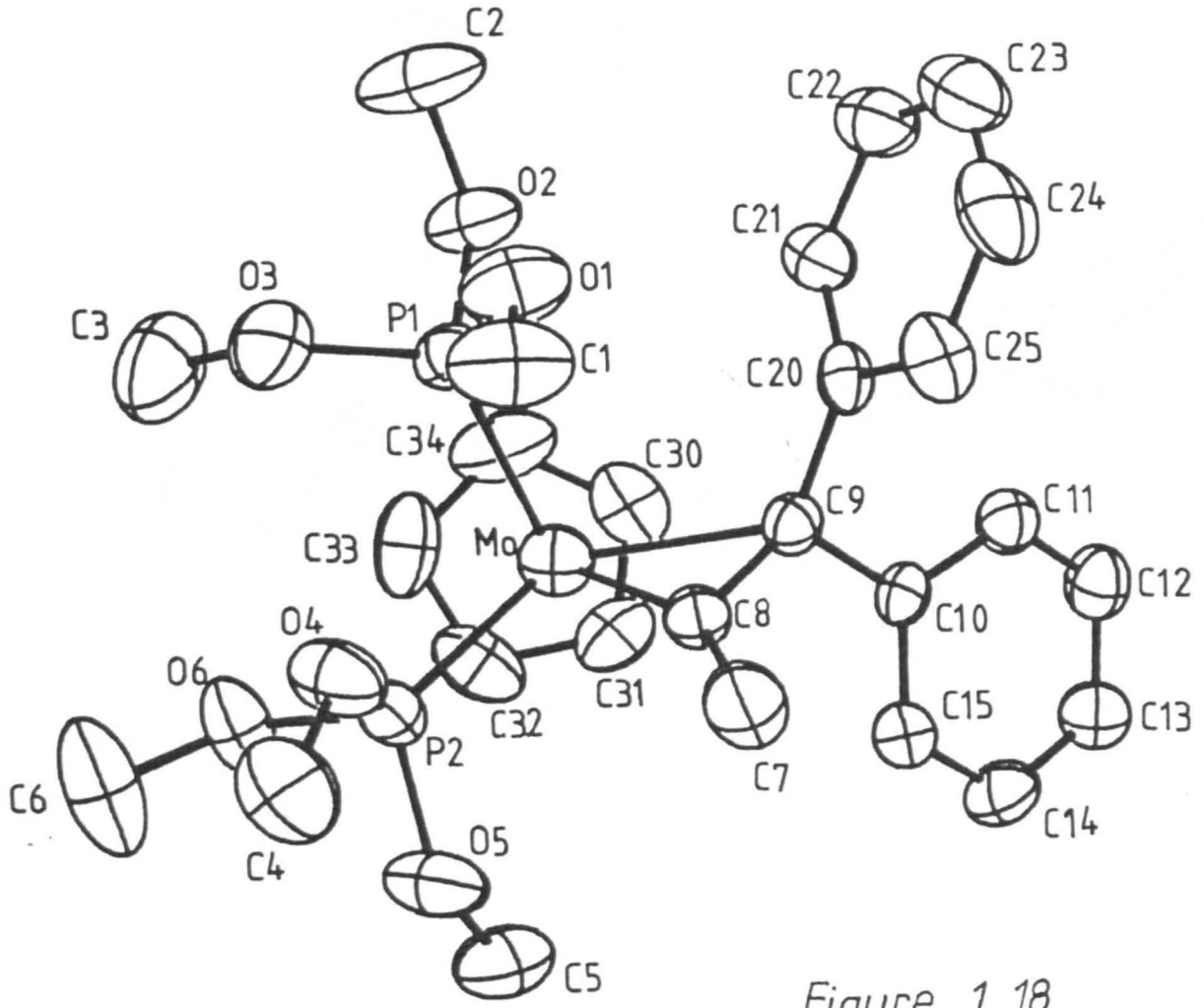

C2
C23
C22
O2
C24
C21
O3
O1
C3
P1
C1
C25
C20
C34
C30
C9
C11
C33
Mo
C12
C8
C10
O4
O6
C31
C15
C13
C32
P2
C7
C6
C14
O5
C4
C5

Figure 1.18

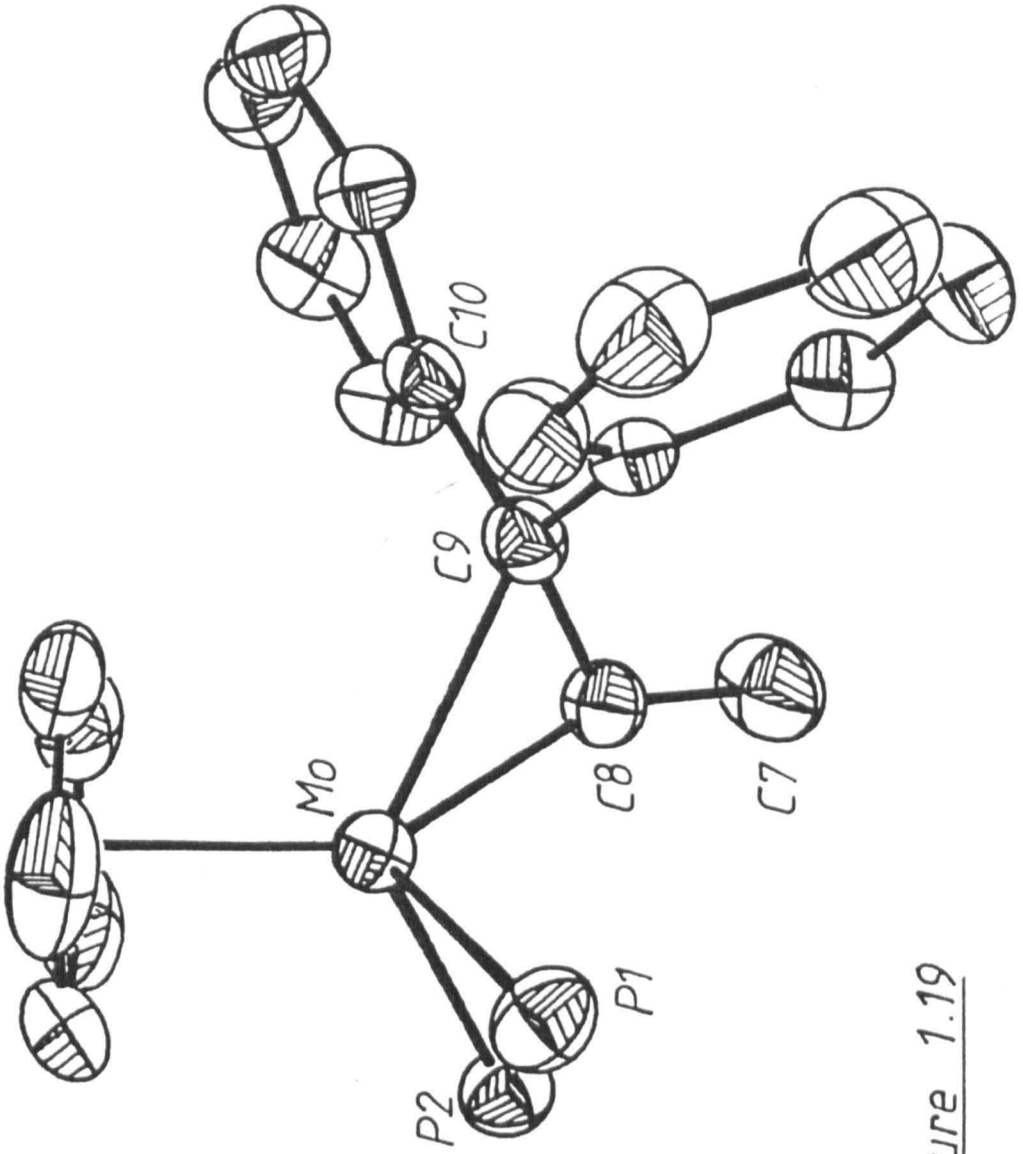


Figure 1.19

occupy the sterically demanding axial site if an orientation similar to (18) and (21) was adopted. Conversely the orientation adopted by (V) might be expected to be disfavoured for (18) and (21) because the Cα substituents are phenyl and ^{t}butyl.

Despite the change in orientation of the vinyl ligand its bond lengths are not dissimilar to those found for (18) and (21), (Table 1.5). The carbene carbon C(8) is 1.965(4)Å from the molybdenum and the β-carbon C(9) 2.248(4)Å. The β-carbons in (18) and (21) are slightly farther from the metal at 2.300(3)Å and 2.282(3)Å, respectively. The C(8)-C(9) bond of 1.465(5)Å is longer than the corresponding bonds in (18) and (21). This may be interpreted in terms of greater π-back-bonding from the metal to the vinyl in (V).

Comparison of the Mo-P bond lengths in the three complexes would appear to back this up. The average Mo-P distances in (18) and (21) are 2.333(1)Å and 2.344(1)Å, (with no great asymmetry between the two phosphites). In (V) though, Mo-P(1) = 2.398(1)Å and Mo-P(2) = 2.367(1)Å, considerably longer and showing distinct asymmetry.

The asymmetry in the Mo-P lengths may be due to electronic effects; the P(2)-Mo-C(9)-C(8) torsion angle is 0·5°, the vinyl ligand has a skew orientation similar to the acetylene ligand in (I) and once more the phosphorus with which it is 'aligned' is the one more tightly bound to the metal.

The bond lengths about the carbene carbon C(8) sum to 359.9°, so that the carbon atom C(7) of its methyl substituent lies in the plane of the metallacyclopropene ring. The C(7)-C(8)-C(9) angle is 126.0(4)°, which is more acute than the bend-back angle found in acetylene

complexes or that of 134.7(5)° at the iminoacyl carbon of (32), which also has a methyl substituent.

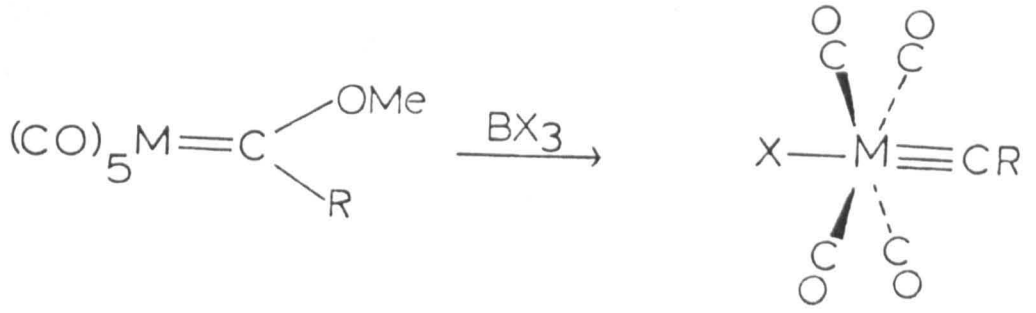
Section 1.2

Formation of the Alkylidyne Complex $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

Introduction

The formation of the alkylidyne complex (VI) by treatment of the acetylene complex (I) with hydride, or the thermolysis of the η^1-vinyl complex (II) was without precedent.[33,34]

All other reported syntheses of mononuclear carbyne complexes have involved carbene (or carbenoid) precursors.[67] Fischer et al. produced the first carbyne complexes (35) in 1973 by reaction of the carbenes $[M(CO)_5\{C(OMe)R\}]$ with boron trihalides.[68]

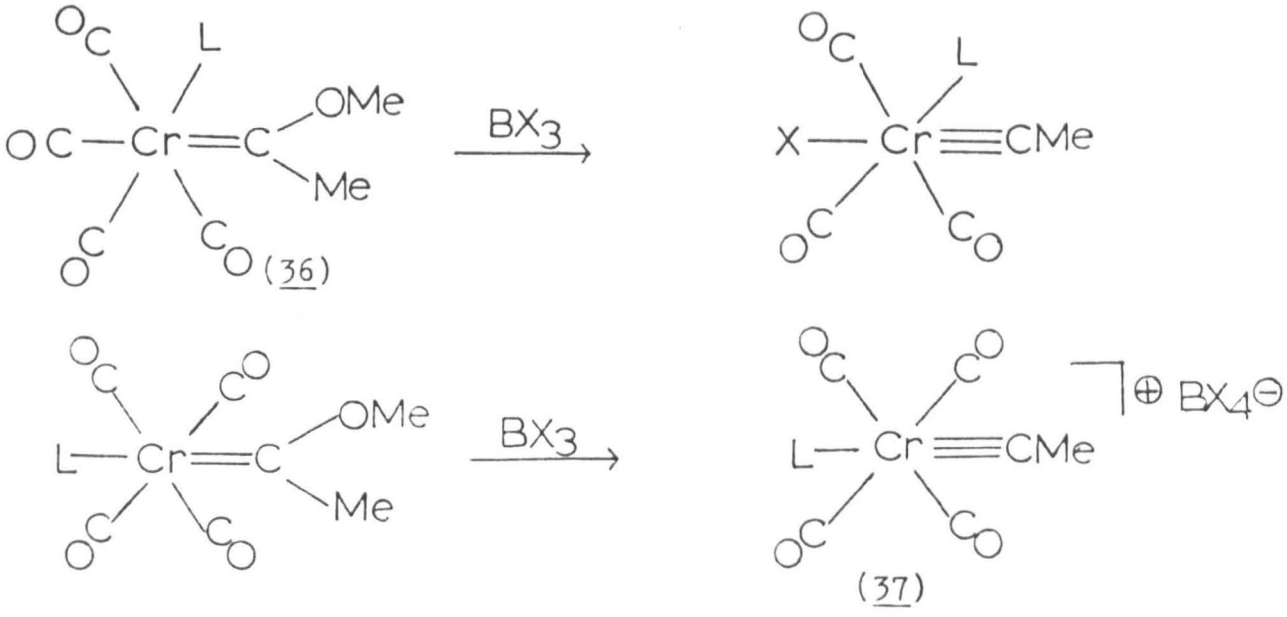


M = Cr,Mo,W R = Me,Et,Ph (35)

This reaction has been found to be quite general and may be carried out for a wide range of R groups such as alkynyl, silyl or even ferrocenyl. Other Lewis acids, e.g. aluminium or gallium halides may be employed instead of $[BX_3]$. The compounds (35) are in general thermally unstable above -20°c.[69-72]

If the cis-PMe_3, $AsMe_3$, or $SbMe_3$ substituted carbenes (36) are treated with boron trihalides the carbynes produced are as expected, with the halide trans- to the carbyne ligand, and with one of the equatorial carbonyls now substituted by the group V donor ligand.[73]

If the isomeric trans- substituted carbenes are used though, the products are the cationic carbynes (37).[74]

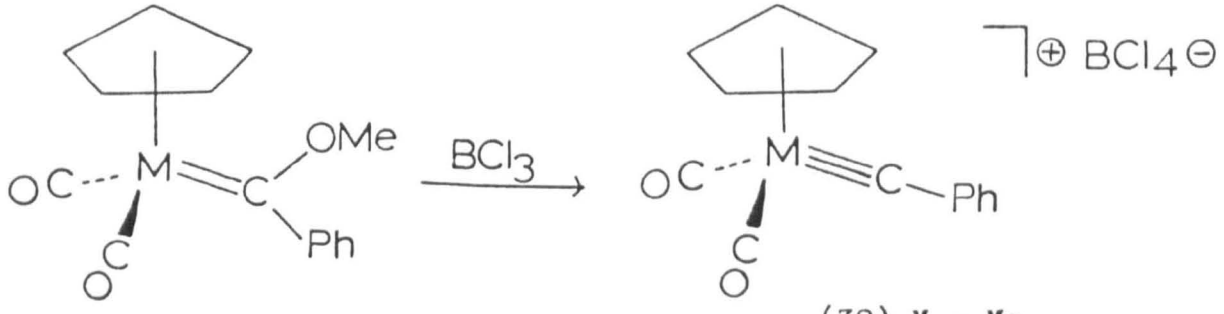


(36)

(37)

Thus if the ligand trans to the carbene is a good donor, it is not lost during the reaction.

The method may also be employed for other systems, e.g. in the synthesis of the cationic manganese and rhenium carbynes (38) and (39) which are analogous to (VI).[75,76]

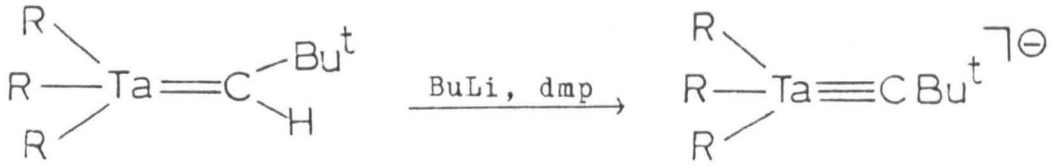


(38) M = Mn

(39) M = Re

The Fischer approach involves the preparation of methoxy substituted carbene complexes from metal carbonyls,[77] the wide range of the latter indicating the great potential of this synthetic route.

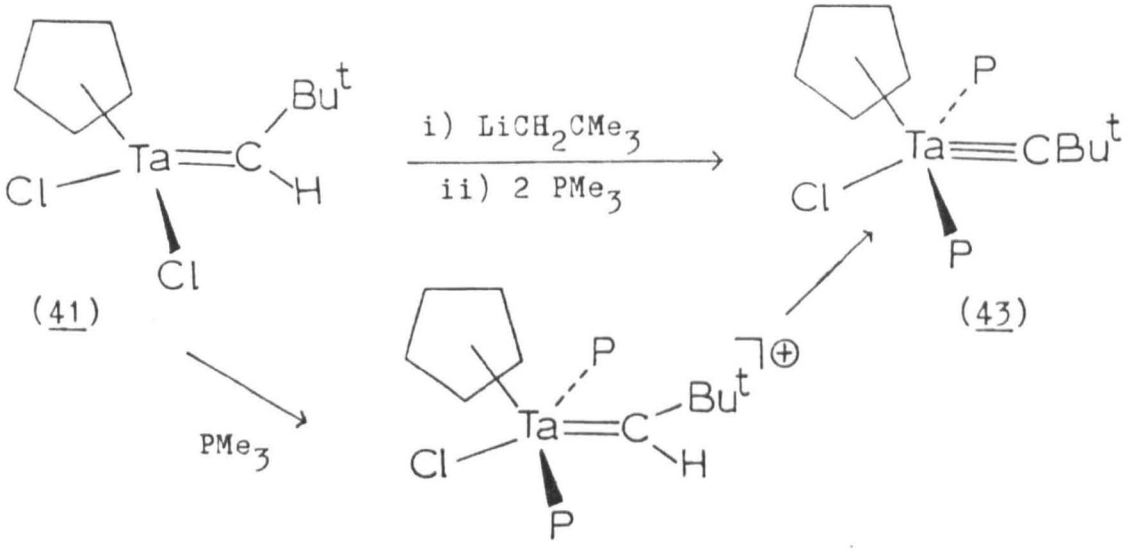
Schrock and coworkers have developed another route to carbyne complexes albeit again involving carbene precursors. Attack of base on the neopentylidene complex $[Ta(CHCMe_3)(CH_2CMe_3)_3]$ yields the carbyne (40).[78]



(40)

dmp = N,N-dimethylpipirazine

Similarly the neutral alkylidyne complex (43) is produced by treatment of the cationic carbene (42) with the ylide $[Ph_3P{=}CH_2]$ which functions as a base.[79]



(41) (43)

(42)

Alternatively (43) may be obtained from (41) by consecutive treatment with neopentyllithium and phosphine.

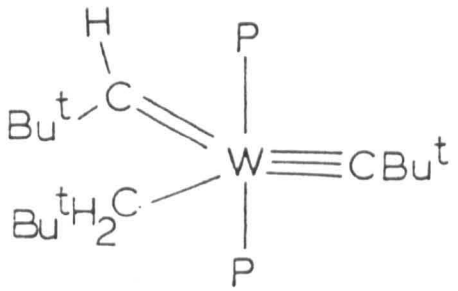
Reaction of molybdenum and tungsten chlorides with neopentyllithium results in the formation of alkylidyne complexes (44) and (45), neutral analogues of (40).[80]

$$MCl_n \xrightarrow{n\,LiCH_2CMe_3} [M{\equiv}CCMe_3(CH_2CMe_3)_3]$$

M = Mo, n = 5 (44)

M = W, n = 6 (45)

Addition of $[PMe_3]$ to the tungsten complex (45) yields an interesting species, (46), which possesses alkyl, alkylidene and alkylidyne ligands.[81,82]



(46)

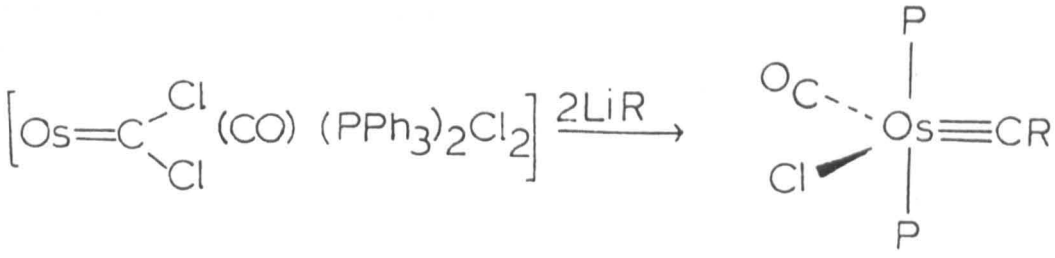
The first synthesis of a mononuclear methylidyne complex was also carried out by Schrock et al.[83] (see below).

$$[WCl_2(PMe_3)_4] \xrightarrow[ii)\ TMEDA]{i)\ 2AlMe_3} Cl{-}W{\equiv}CH\ (P_4)$$

(TMEDA = N,N,N',N'-tetramethylethylenediamine)

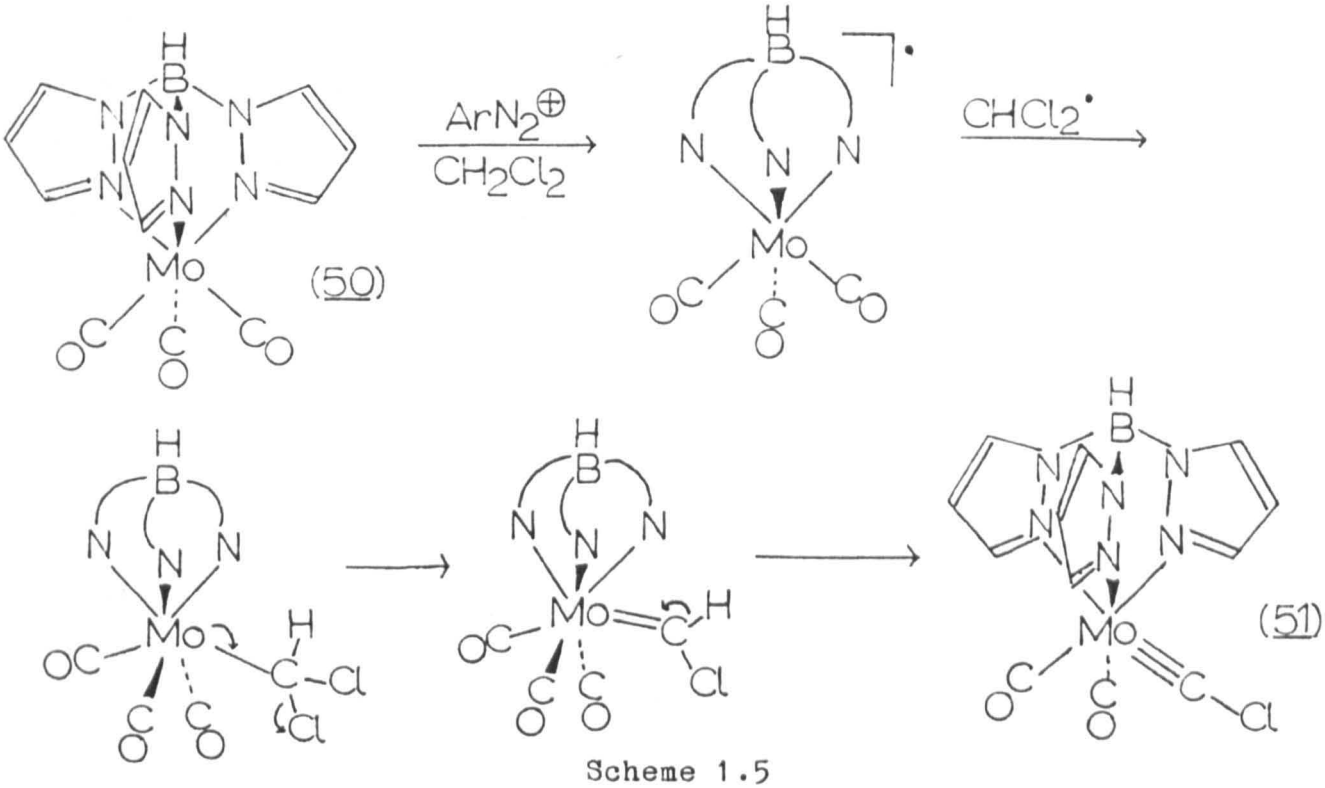
(47)

Reaction of the dichlorocarbene complex (48) with various lithium aryls gave access to the first osmium carbynes (49).[84]



(48) (49)

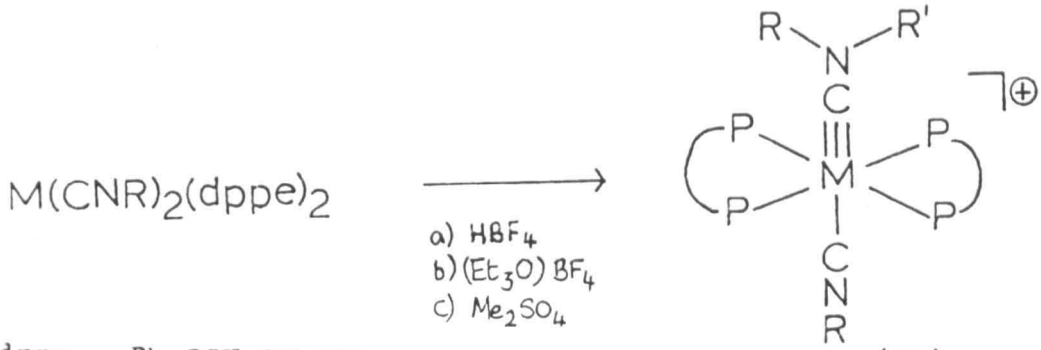
The first chlorocarbyne complex was serendipitously obtained by Lalor et al.[85] upon reaction of (50) with aryldiazonium salts in methylene chloride. A radical mechanism was proposed (Scheme 1.5).



Scheme 1.5

Further work has since appeared, demonstrating the synthetic utility of the chlorocarbyne as a precursor for other heteroatom-carbyne species.[86]

Other hetero-atom substituted alkylidynes have been produced by electrophilic attack on isocyanide and thiocarbonyl complexes; Chatt and coworkers have synthesised aminocarbyne complexes (52) by the reaction below.[87-89]

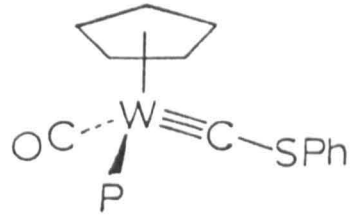


(52)

dppe = $Ph_2PCH_2CH_2PPh_2$

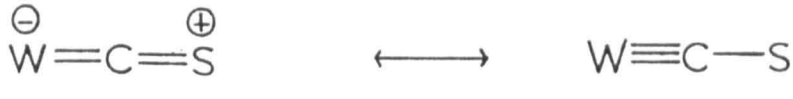
M = Mo,W R = Me,Bu^t,aryl R' = Et,Me,H

Angelici has synthesised a neutral thio analogue of (52) by attack of $[MeSO_3F]$ on $[W(CO)(CS)(dppe)_2]$, giving the salt $[W(CO)(CSMe)(dppe)_2][SO_3F]$.[90] Similarly nucleophilic attack on a thiocarbonyl complex yielded (53), containing an arylthio- substituted carbyne ligand.



(53)

The structure of (53) indicates that resonance form b) is dominant.



a) b)

The carbyne syntheses above all involve precursors with carbene or carbene-like ligands (e.g isocyanide, thiocarbonyl). In the case of carbenes, the carbyne is formed upon loss of one of the carbene

substituents, typically a hydrogen or an alkoxy group. Alternatively hetero-atom substituted carbyne ligands may be produced by alkylation of the s-hetero-atom of isocyanides and thiocarbonyls. This latter approach implicating the potential of vinylidene ligands for alkylidyne synthesis, evidence for which will be presented in Section 1.4.

Crystal Structure of the Alkylidyne Complex (VI)
$[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

The characterisation of the complex (VI) as a carbyne complex was based on spectroscopic evidence.[34] The mass spectrum showed the parent ion to have a peak (^{96}Mo) at 492. The ^{31}P n.m.r. showed a singlet, the ^1H n.m.r. indicated that this was due to two equivalent $[P(OMe)_3]$ groups, the protons of which appeared as a 'virtual' triplet. Together with single resonances for the ^{t}butyl and cyclopentadienyl protons there was a triplet at 2.4ppm, attributed to the methylene group of a neopentylcarbyne ligand. The crucial evidence for this formulation was the appearence of a low-field triplet in the ^{13}C n.m.r. of (VI) at 299ppm.[34] This resonance was in the region of other alkylidyne carbon chemical shifts.[91]

Confirmation of this structure for (VI) was desirable for two main reasons i) the unusual method of synthesis of (VI) and ii) the molecule was to be important as a starting material for further synthesis.

Crystals of (VI) were grown from hexane at -78°c as yellow prisms. A specimen of dimensions 0.55 x 0.5 x 0.2 mm was used for data collection. The structure was refined to a final discrepancy index, R = 0.026, and completely confirmed the spectroscopic formulation.

Compound (VI) crystallised with two independent molecules in the asymmetric unit. No important geometrical differences were found between the two and so averaged values of structural parameters are given in the discussion below.

The geometries of the molecules together with their labelling schemes are illustrated in Figures 1.21 and 1.22.

The compound has a three-legged pianostool geometry typical of $[CpML_3]$ complexes. As proposed the molybdenum is bonded to two trimethylphosphites, a neopentylcarbyne ligand and a cyclopentadienyl group.

The carbyne is linear; Mo-Cα-Cβ = 175° indicating sp hybridisation at the carbyne α-carbon. The Mo≡C bond is 1.798(2)Å long. This is similar to that found in the phenylcarbyne complex $[Mo(CPh)(CO)_4Re(CO)_5]$ (Mo-Re) of 1.835(3)Å.[92] The chlorocarbyne species (51), for which there were three crystallographically independent molecules had a longer Mo≡C triple bond (av. = 1.894(10)Å). This might be due to the conjugative effect of the chloro group reducing the degree of metal-carbon π-bonding. A degree of carbonyl/chlorocarbyne disorder might also be present which would tend to lengthen the observed Mo≡C distance.[86]

In common with compounds (I) through (V), the molecule (VI) has potential mirror symmetry. In the solid state this is not found, the ^{t}butyl group of the carbyne lying to one side of the molecule. There is slight asymmetry in the Mo-P distances. The average length of the four independent Mo-P bonds is 2.329(1)Å. This value is smaller than for any of the molybdenum-phoshite bonds in (I), (II), (IV) or (V). This would indicate the electron rich nature of (VI), although the lower coordination number of the metal in (VI) may also be a factor.

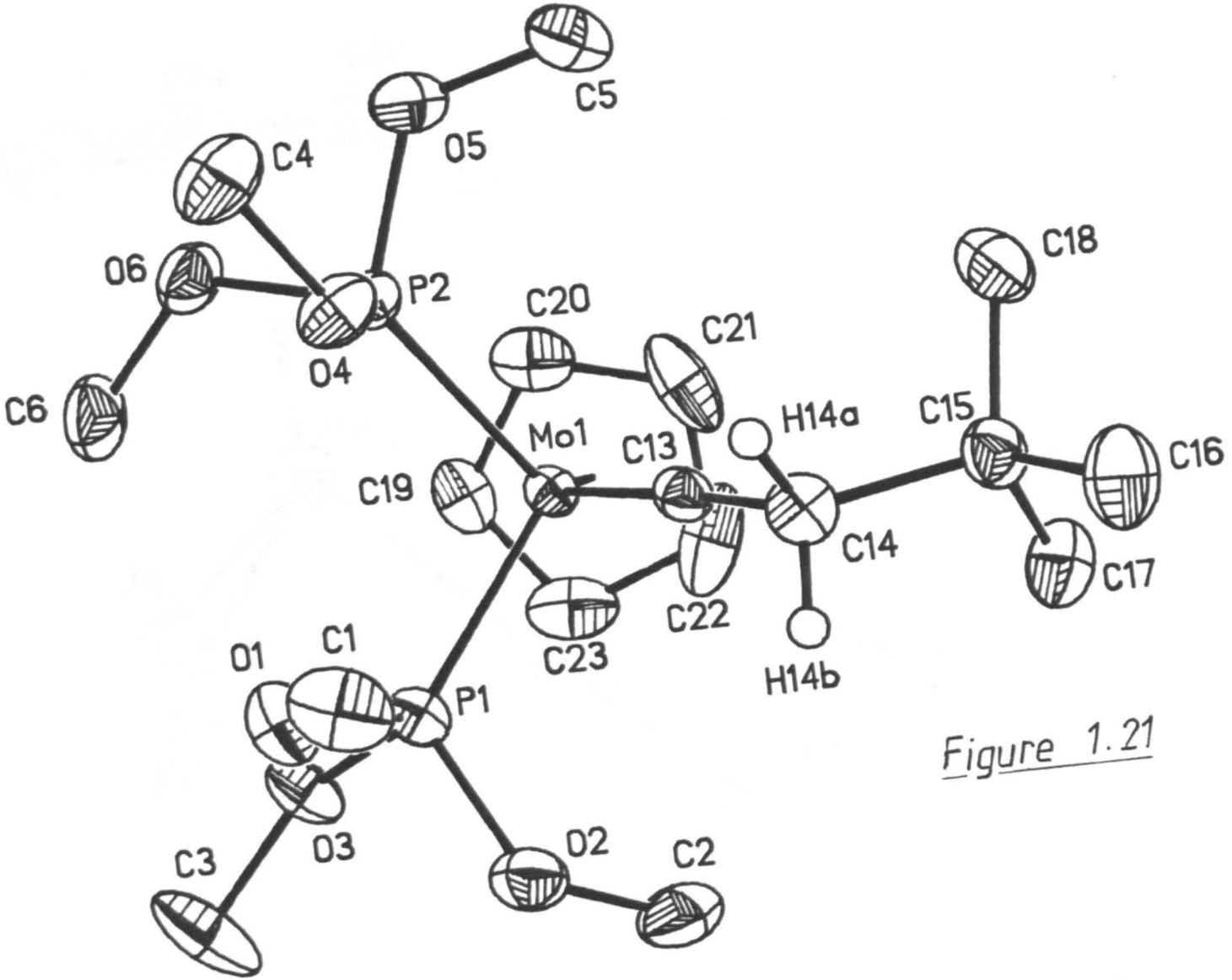

C5
O5
C4
O6
P2
C20
C21
C18
O4
C6
Mo1
C13
H14a
C15
C16
C19
C14
C17
C22
C23
H14b
O1
C1
P1
O3
O2
C3
C2

Figure 1.21

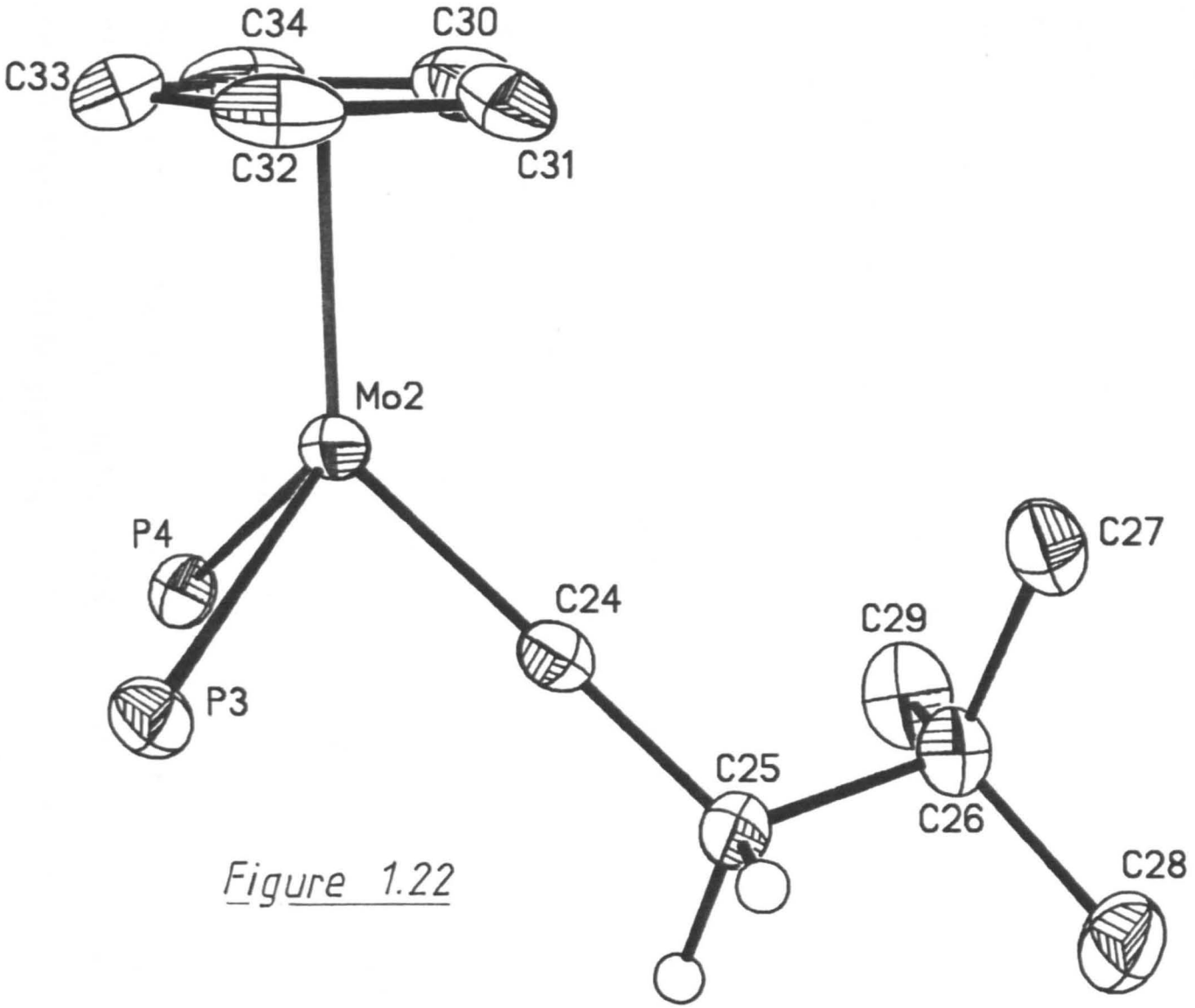
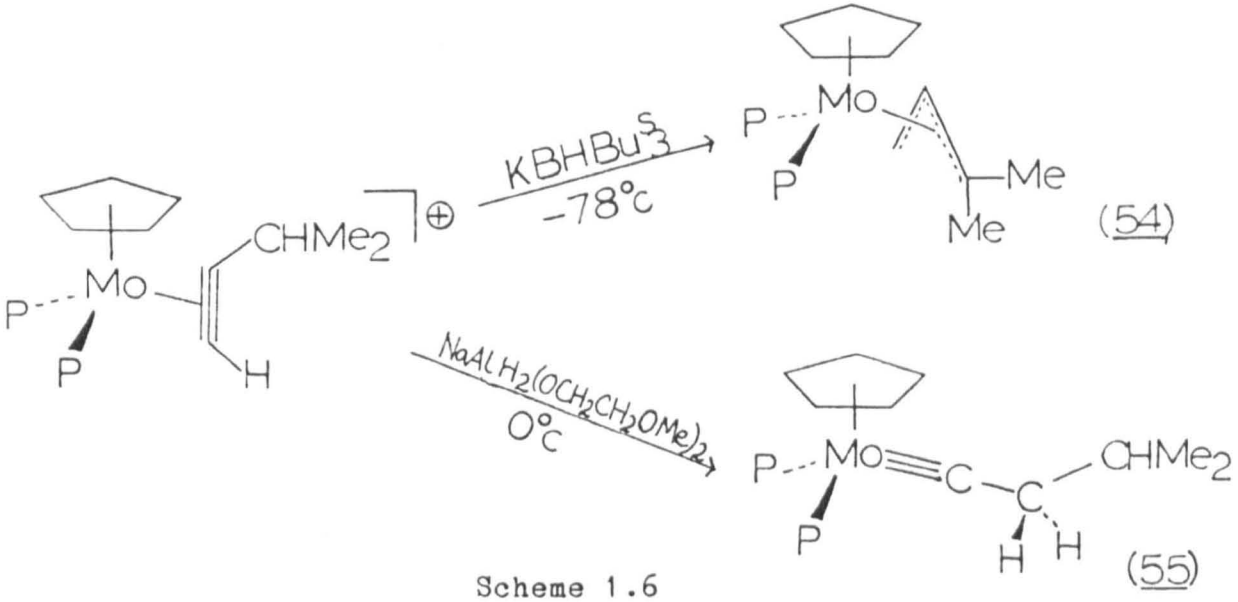


Figure 1.22

The two $[P(OMe)_3]$ ligands and the carbyne form a roughly orthogonal set. The inter-phosphite angles averaging 93.5(1)° and the angles between the phosphites and the carbyne 88.3(1)°. Thus the complex may be described as pseudo-octahedral, with the cyclopentadienyl ligand occupying the remaining three sites.

Mechanism of Formation of $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

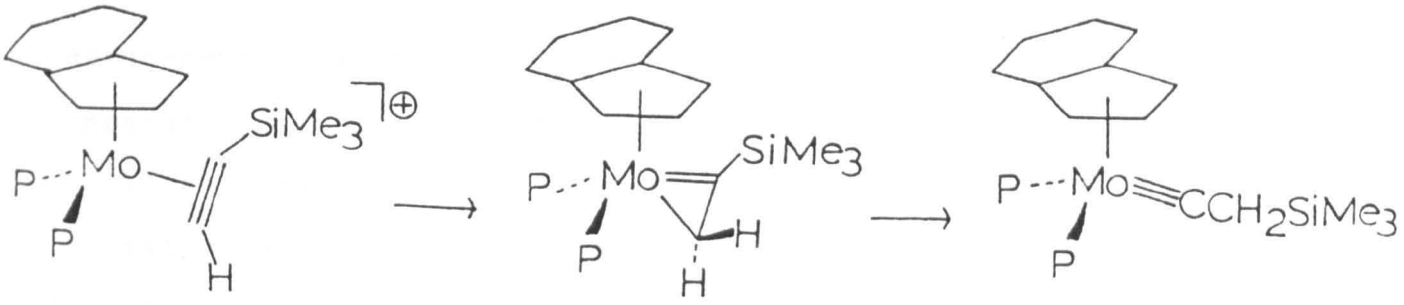
Attack of hydride on other terminal acetylene complexes analogous to (I) was also found to yield alkylidyne complexes. The isopropyl analogue to (I), $[Mo(HC{\equiv}CPr^i)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, which possesses both α- and β- acetylene protons gave either the π-allyl complex (54) or the alkylidyne (55) depending on the reaction conditions. (Scheme 1.6).[66]



Scheme 1.6

The tungsten analogue of (VI) was formed in 40% yield on addition of the aluminium hydride $[(CH_3OCH_2CH_2O)_2AlH_2][Na]$ at 0°c to the alkyne complex $[W(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ in the presence of trimethylphosphite, no stable η-vinyl intermediate being isolated.[93]

However, reaction of $[Mo(HC{\equiv}CSiMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ with $[Bu^s{}_3BH][K]$ at -78°c, yielded a blue-green crystalline product (VII) thermally stable in the solid state, but which rearranges cleanly over a period of 1 hr. at 0°c in toluene solution to the yellow alkylidyne complex (56).[66]



(VII) (56)

Examination of the ^{13}C n.m.r. spectrum of (VII) revealed a low-field resonance at 276.5ppm, assigned to an alkylidene carbon, and a peak at 23.9ppm thought to be due to a methylene carbon. On the basis of spectroscopic information (VII) was believed to have the η^2-vinyl structure shown above.[66] The mechanistic importance of (VII), as a direct precursor to the alkylidyne (56), rendered confirmation of this by crystal structure analysis highly desirable.

Accordingly several crystals were mounted in capillary tubes under an argon atmosphere and a suitable specimen chosen for the x-ray diffraction study. This was carried out at low temperature (-50°c) after experience of crystal decomposition in the x-ray beam at room temperature. This had the added benefit of increased structural accuracy, all atoms including hydrogens, were located, and the final R = 0.026.

The x-ray results confirmed the structure of (VII) as the η^2-vinyl complex $[Mo{=}\overline{C(SiMe_3)}CH2\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$. Figures 1.23 and 1.24 show the molecular geometry of (VII) viewed both parallel and normal to the plane of the indenyl group.

Quantitative structural comparisons between (VII) and the other η^2-vinyl complexes (18), (21) and (V) are rendered difficult a) by the replacement of a cyclopentadienyl group by an indenyl and b) the lower temperature of data collection for (VII).

It is clear that the orientation of the η^2-vinyl ligand is similar to that observed for compounds (18) and (21) rather than that of (V). Thus the carbene carbon C(8), which bears the bulky trimethylsilyl substituent is in a position away from the phosphite groups. The saturated or β-carbon possesses only hydrogen substituents, so that adoption of this orientation by the η^2-vinyl gives rise to no severe interactions.

The bond lengths about the metallacyclopropene ring are similar to those found for (18) and (21); the Mo-C(8) bond is 1.957(3)Å and the Mo-C(7) bond 2.260(4)Å. The ring is completed by theC(7)-C(8) bond of 1.436(5)Å.

The possibility of $p\pi$-$d\pi$ bonding between the carbene carbon C(8) to the silicon of its $SiMe_3$ substituent was considered. There is little structural evidence that this is occurring to a significant degree. Whilst the Si-C(8) distance of 1.850(4)Å is found to be shorter than the average Si-C(methyl) bond length of 1.877(4)Å, a substantial part of this discrepancy is due to the radial contraction observed for sp^2 versus sp^3 carbon. The molybdenum-phosphorus bond lengths of 2.351(1)Å and 2.359(1)Å are intermediate with those of (18), (21) and (V).

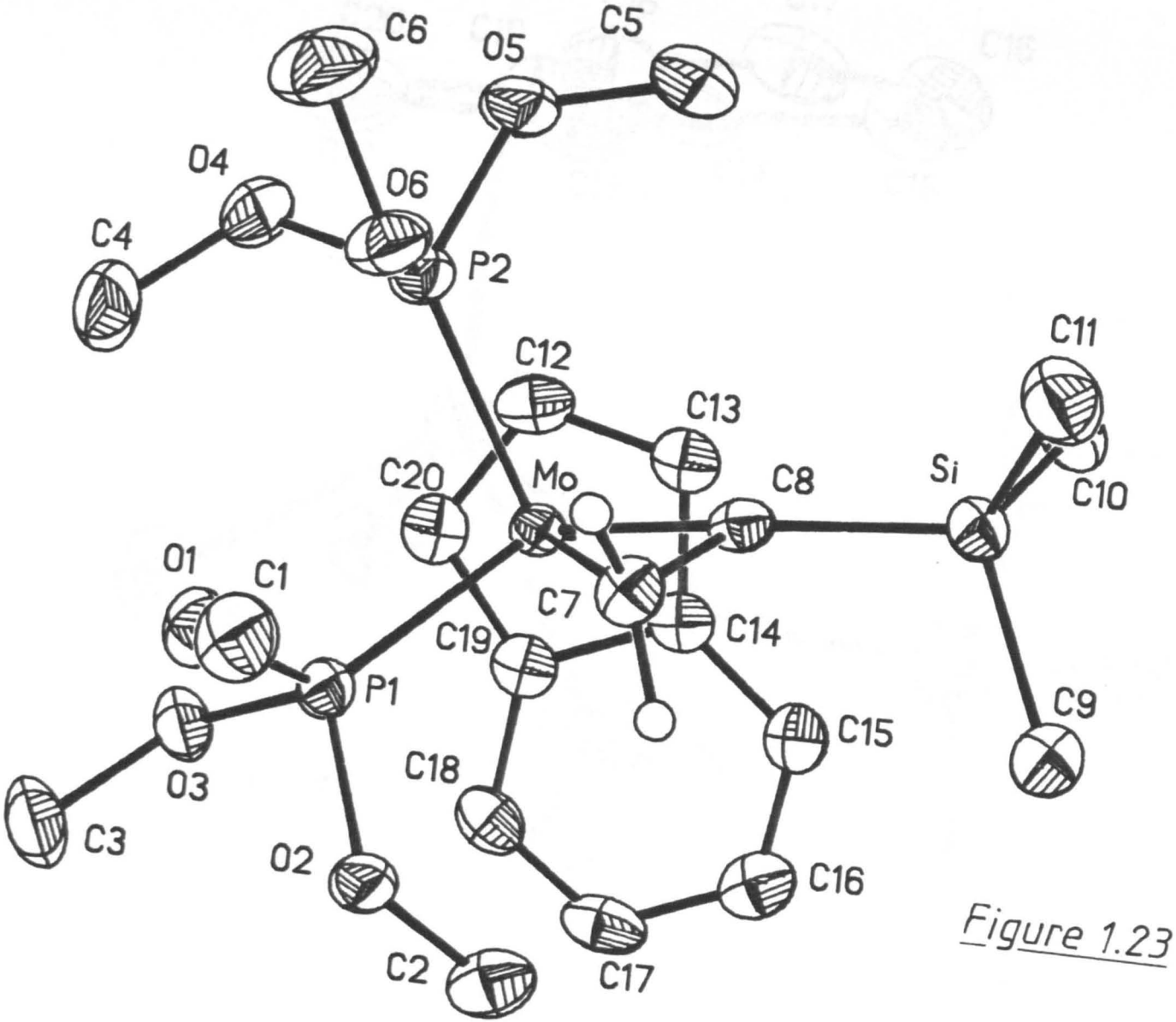

C6
O5
C5
O4
O6
C4
P2
C12
C11
C13
C20
Mo
C8
Si
C10
O1
C1
C7
C14
C19
P1
C9
C15
O3
C18
C3
O2
C16
C2
C17

Figure 1.23

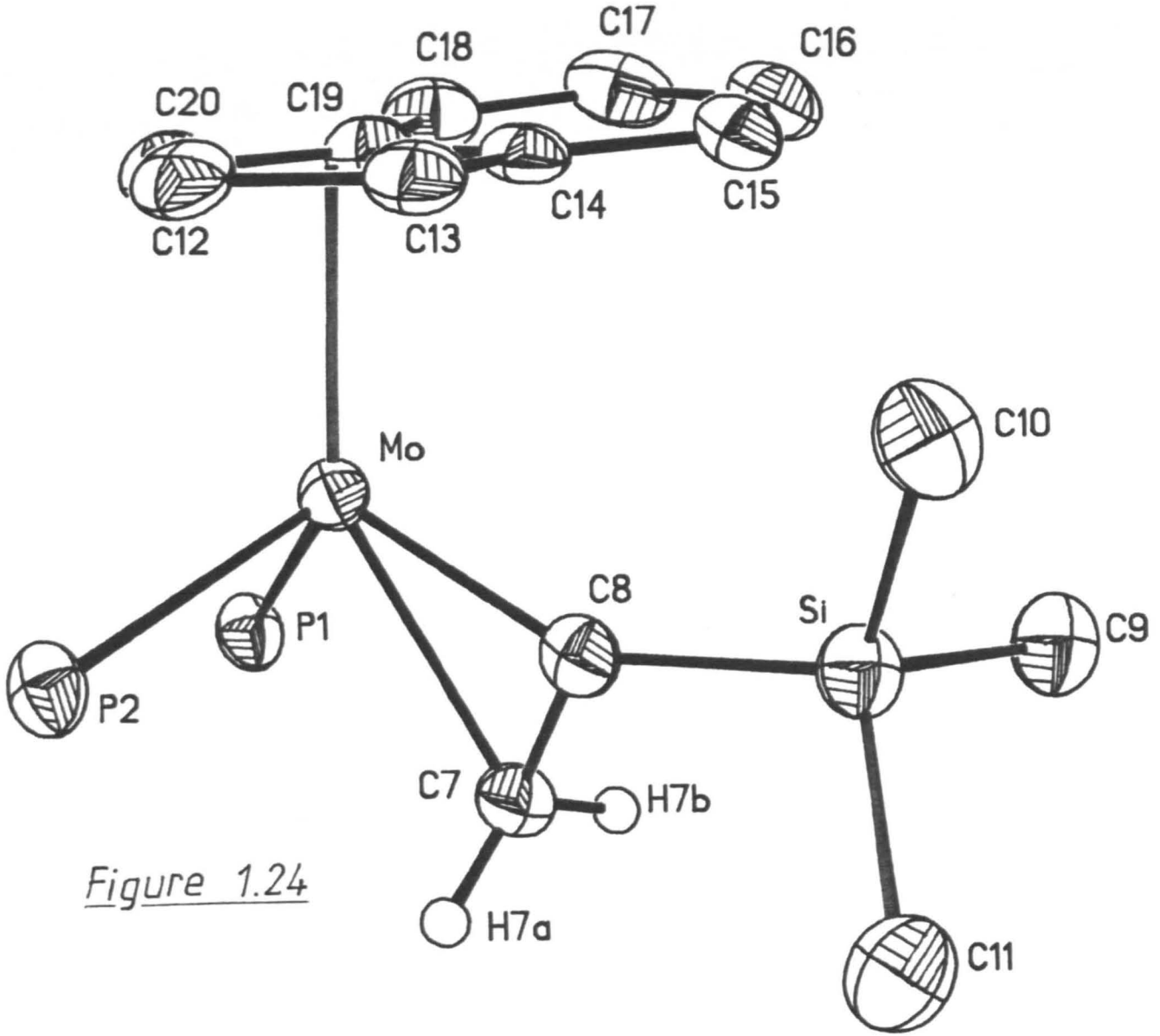
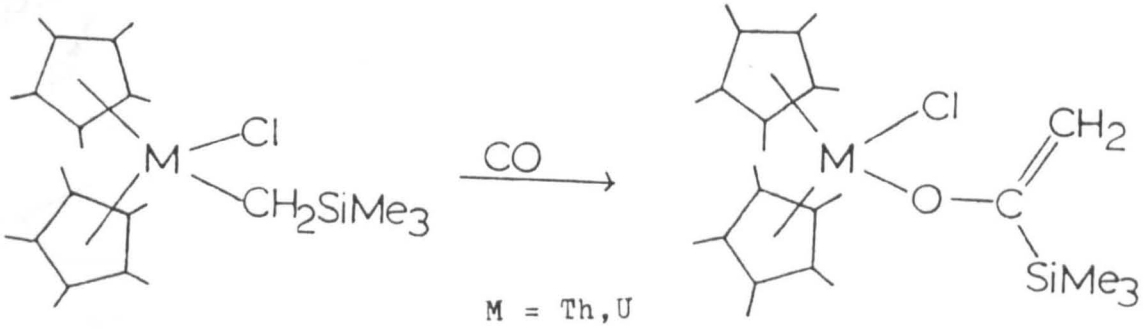

C17
C18
C16
C20
C19
C14
C15
C12
C13
Mo
C10
C8
Si
C9
P1
P2
C7
H7b
H7a
C11

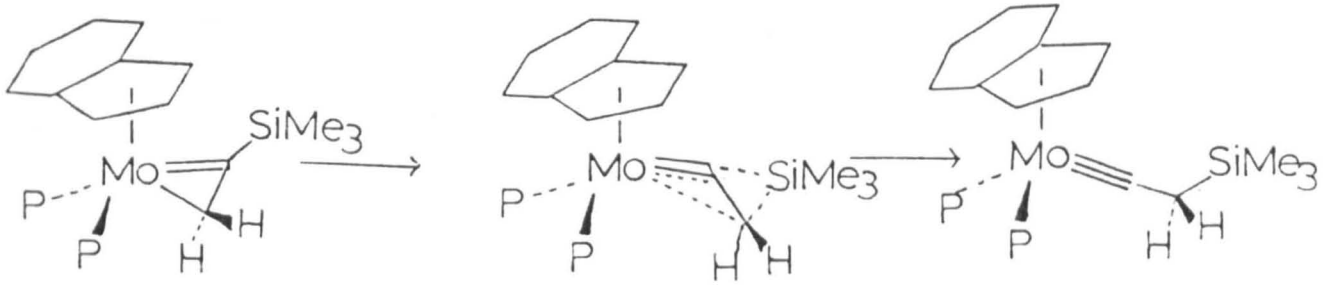
Figure 1.24

Mechanism of Alkylidyne Formation

The rearrangement of (VII) into the carbyne (56) involves a formal 1,2-trimethylsilyl shift, from the unsaturated alkylidene carbon C(8) to the saturated methylene carbon C(7). Silyl migrations are well documented in organic chemistry.[94,95] A 1,2-trimethylsilyl shift has been observed in organoactinide chemistry by Marks et al.[96]



In the case of Marks's reaction though, the $SiMe_3$ group is thought to migrate from a saturated carbon to a carbene centre.

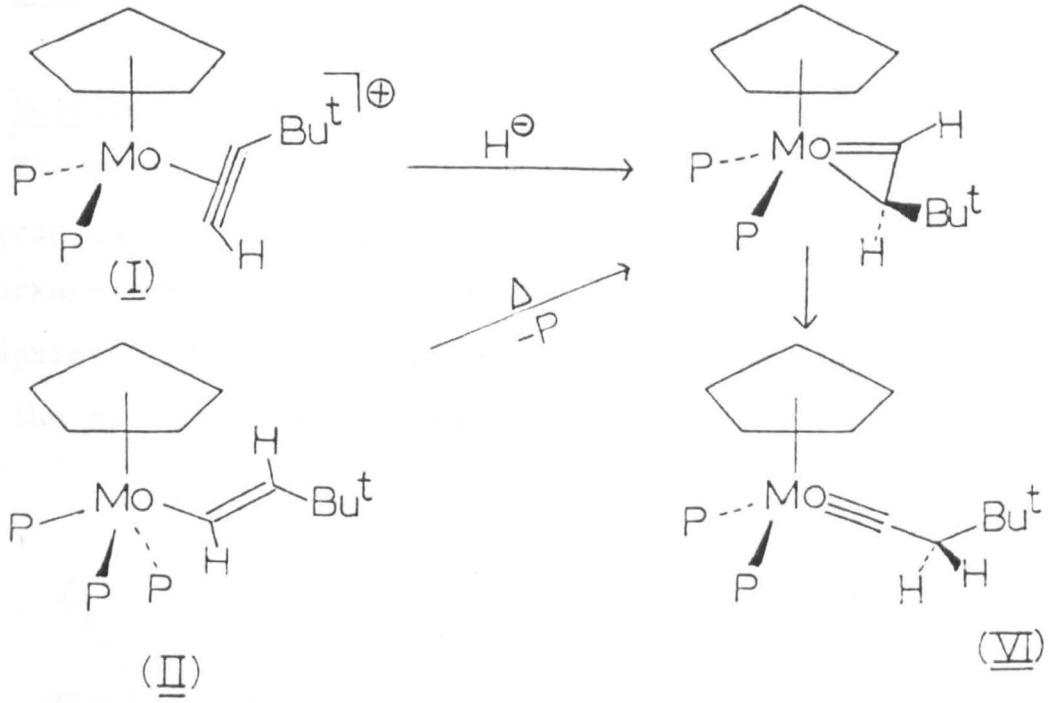


(VII) ⟶ (56)

Conversion of (VII) to (56) thus requires the opening of the Mo-C(8)-C(7) angle as the Mo-C(7) bond is cleaved, whilst the silicon migrates from the α- to the β-carbon of the vinyl ligand.

Formation of the alkylidyne (VI), $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ is thought to proceed similarly via a η^2-vinyl intermediate which has so far eluded detection. The forcing conditions (80°c) used in the

preparation of (VI) from (II) are most probably neccessary for dissociation of the third [$P(OMe)_3$] ligand rather than to effect hydrogen migration.



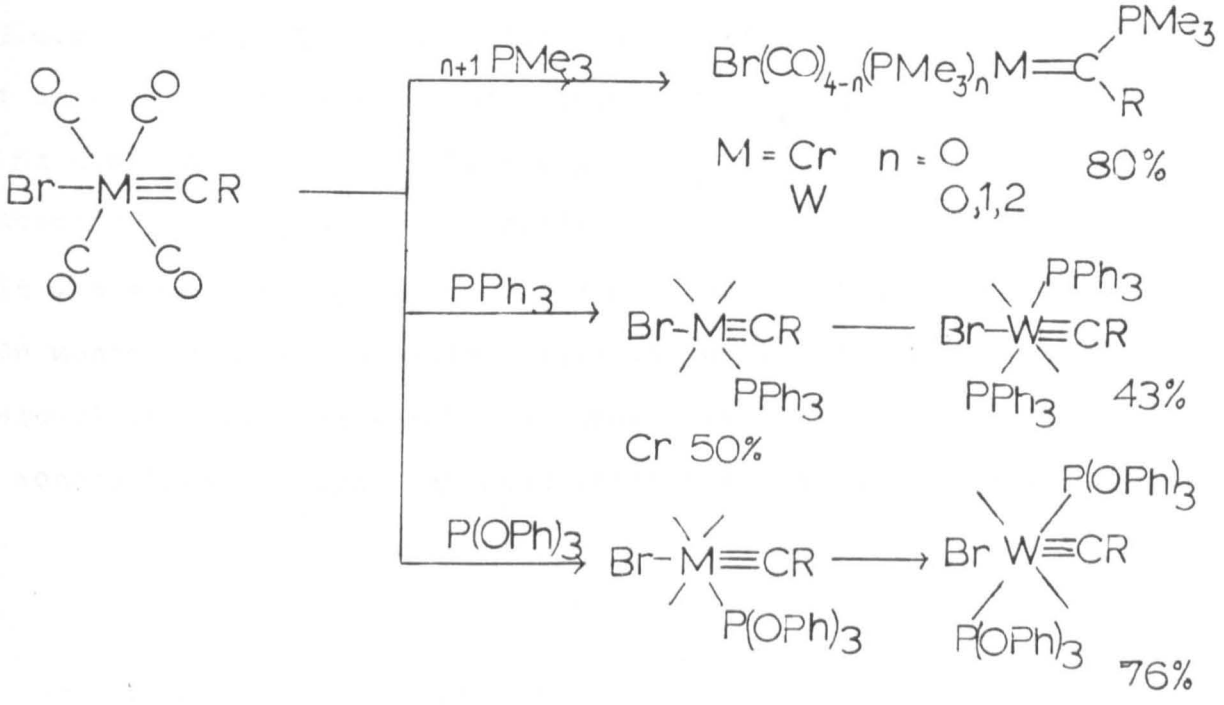
Scheme 1.7

Section 1.3

The Chemistry of the Alkylidyne Complex (VI) $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

Introduction

The reactivity of both neutral and cationic carbyne complexes towards nucleophiles has been extensively studied by Fischer and coworkers. Their results have been reviewed.[97] Reaction of carbynes with phosphines led to a variety of products, dependent on both the phosphine and the metal complex. (Scheme 1.8)

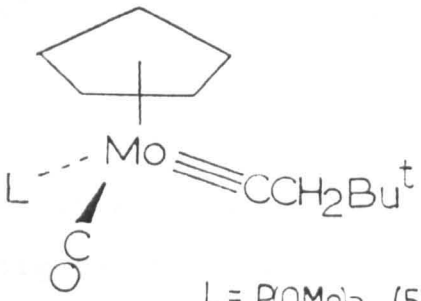


Scheme 1.8

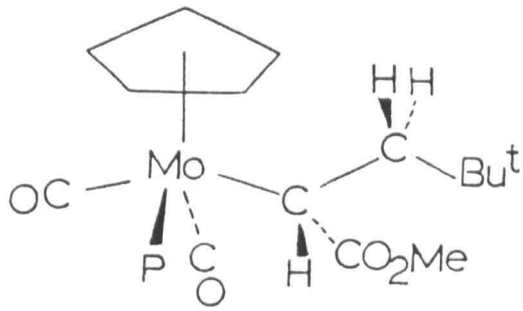
Fenske et al have discussed nucleophilic attack on carbyne complexes from a theoretical standpoint.[98]

The alkylidyne complex (VI) has been shown to react with both nucleophilic and electrophilic reagents.[51]

Treatment of (VI) with carbon monoxide (300 atm.,3 days) was not a clean reaction, yielding (57) and (58), the mono- and di-carbonyl derivatives of (VI) together with a number of minor products of which only (59) was characterised.[51]



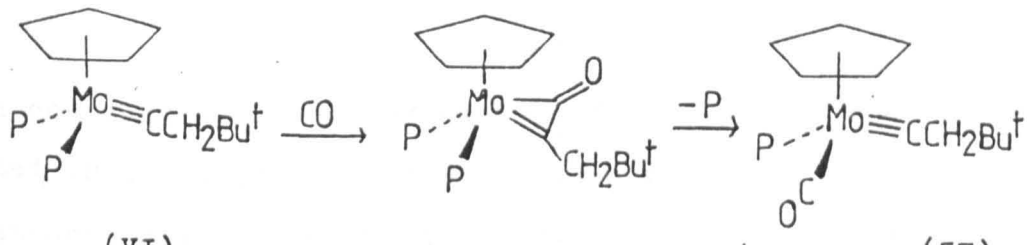
L = P(OMe)3 (57)
L = CO (58)



(59)

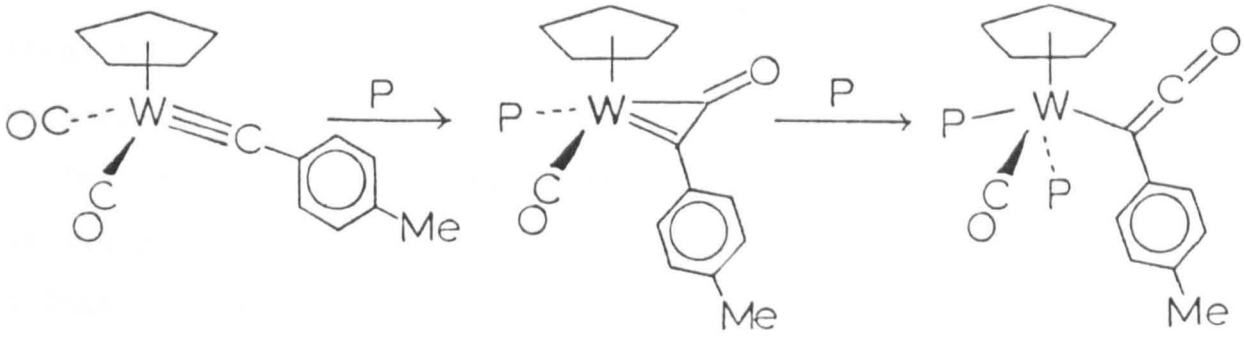
N.m.r. evidence suggested that the [P(OMe)$_3$] ligands do not undergo rapid exchange with free trimethylphosphite in solution.[51] This finding disfavoured a dissociative process for the successive replacement of the phosphite ligands of (VI) in its reaction with CO.

It was thus proposed that (VI) undergoes a cheletropic addition of carbon monoxide to the molybdenum-alkylidyne function, forming a η^2-ketenyl intermediate which rearranges via loss of phosphite to (57). This monocarbonyl-carbyne may then undergo a similar process to give (58).



(VI) (57)

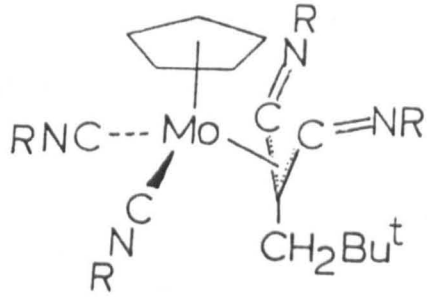
This mechanism is strongly supported by the observation of Kreißl et al of what amounts to the reverse reaction.[99] In an extension of the



(60) (61) (62)

studies of the reactivity of carbyne complexes towards phosphines they investigated the reaction of $[W(CO)_2(CC_6H_4Me)(\eta\text{-}C_5H_5)]$(60) with $[PMe_3]$. Surprisingly a carbonyl migration occurred, and the η^2- and η^1-ketenyl complexes (61) and (62) were formed with one and two equivalents of phosphine respectively.

The reactions of (VI) and its isopropyl and tungsten analogues with isocyanides were also studied. In the case of 2,6-xylylisocyanide the novel isocyanide insertion product (63) was isolated. The nature of this was determined by x-ray crystallography.[93]



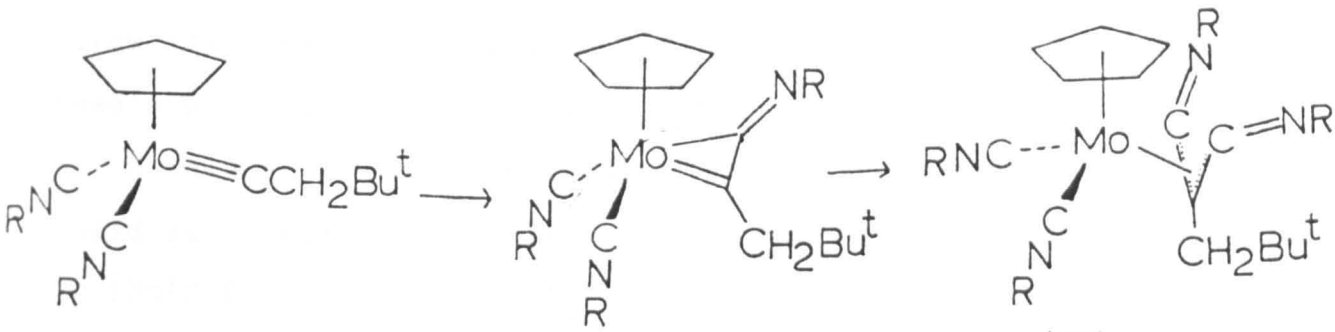
(63)

In contrast treatment of $[M(CO)_4(CPh)Br]$, M = Cr,W, with ^tBuNC resulted in the substitution of a carbonyl ligand by an isocyanide.[100] The cationic alkylidyne $[Mn(CO)_2(CPh)(\eta\text{-}C_5H_5)][BF_4]$ adds ^tBuNC at

the carbyne carbon to form the unstable ionic carbene species $[Mn\{C(Ph)CNBu^t\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$.[101]

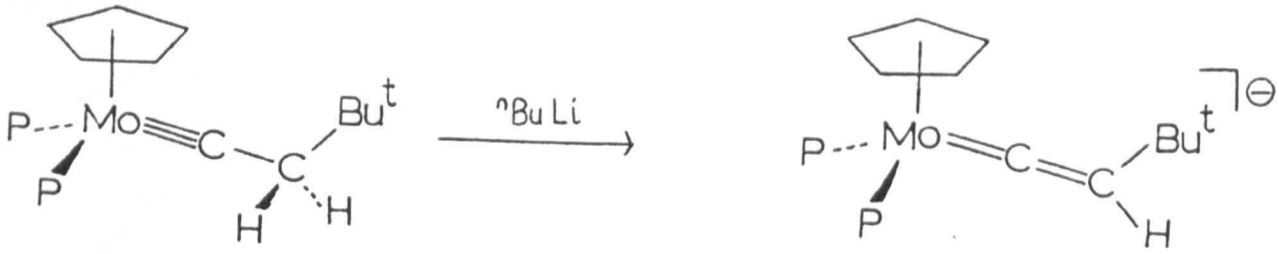
The mechanism of the formation of (63) has been investigated by adding 1, 2, 3 and 4 equivalents of isocyanide to (VI) and monitoring the progress of the reaction by ^1H n.m.r. spectroscopy.[51]

The conclusions of these studies is that initial disubstitution of the two phosphite ligands by the isocyanides occurs in a similar manner to that proposed for CO. Further reaction then takes place either by insertion of coordinated isocyanide into the Mo≡C triple bond or cheletropic attack at this unit by free isocyanide.[93]



(63)

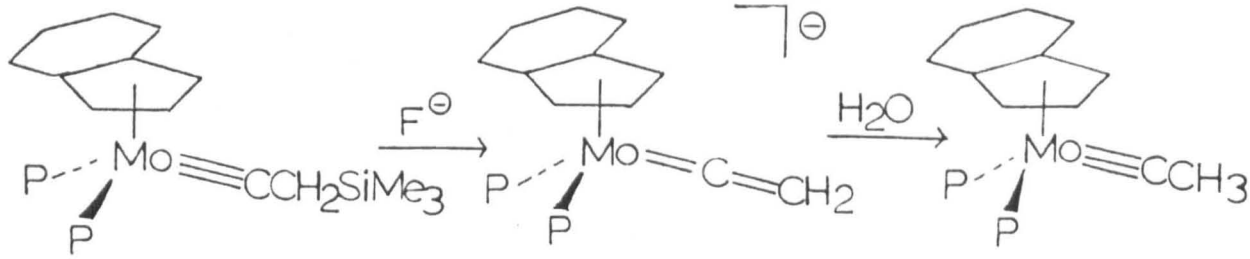
The alkylidyne (VI) has also been reacted with strong base. Treatment of a solution of (VI) with one equivalent of ^nBuLi results in deprotonation at the β-carbon of the carbyne to give the highly moisture sensitive anionic vinylidene species (64).[102]



(VI) (64)

A similar vinylidene anion was proposed to be an intermediate in the

reaction of (56) with fluoride ion, which gave the ethylidyne complex $[Mo(CCH_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (66) as the final product.

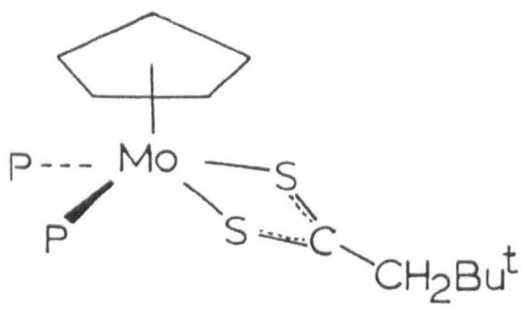


(56) (65) (66)

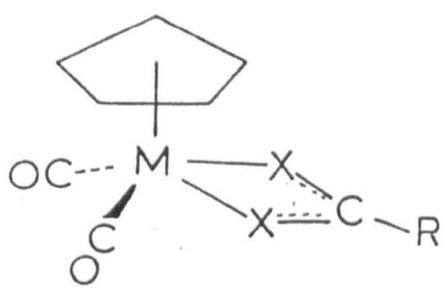
The intermediate (65) was not directly observed but is thought to rapidly pick up protons to form (66). Compound (64) was stable enough to allow its characterisation by ^{13}C n.m.r. spectroscopy. It, too, rapidly reacts with water to give back (VI).

Molecular orbital calculations on carbyne complexes[98] indicate a build up of negative charge on the carbyne carbon. E.H.M.O. calculations on $[Mo(CCH_3)\{P(OH)_3\}_2(\eta\text{-}C_5H_5)]$[103] confirm that a similar charge separation pertains for this model of (VI): net charges of +0.93 and -0.34 were calculated for the molybdenum and carbyne carbon respectively. The α-carbon of the alkylidyne in (VI) might thus be expected to display considerable nucleophilic behaviour.

The reaction of (VI) with elemental sulphur has been studied. This was found to give the product (67).[104]



(67)

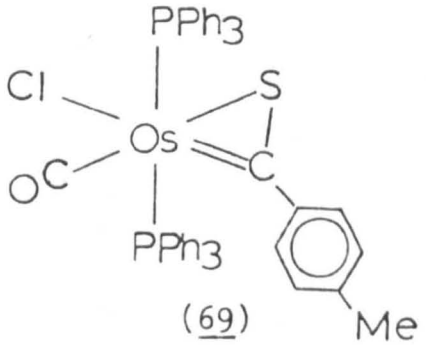


(68)

Similar reactivity was observed for the dicarbonyl analogue of (VI), (58) towards sulphur and selenium, giving the products (68)a and (68)b. The tungsten carbyne (60), $[W(CO)_2(CC_6H_4Me)(\eta\text{-}C_5H_5)]$ yields the analogous (68)c in its reaction with sulphur.[104]

X-ray crystallographic studies were carried out on both (68)a and (68)c. These confirm the incorporation of two sulphur atoms across the metal-carbon triple bond to give dithiocarboxylate moieties.

These reactions are thought to proceed via initial attack of the chalcogen at the carbyne carbon atom and may involve η^2-thioacyl intermediates. Such a species (69), and selenium and tellurium analogues were observed as the final products in the reactions of the osmium carbyne (49) with the chalcogens S, Se and Te.[84]



(69)

The results of further work on the reaction of electrophiles with the carbyne complex (VI) are now reported.

The Protonation of the Alkylidyne Complex (VI) $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

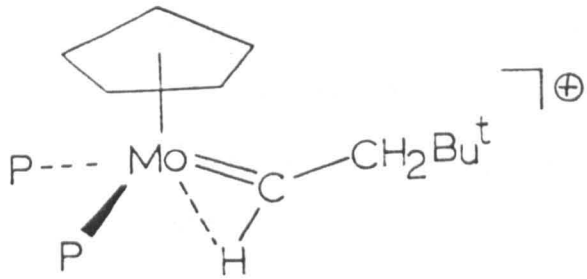
i) Reaction with $[HBF_4]$

In the initial exploration of the chemistry of the carbyne complex (VI) its reaction with hydrofluoroboric acid was investigated.[33,34] Addition of a mixture of $[HBF_4]$(40% aq. soln.) and acetic anhydride

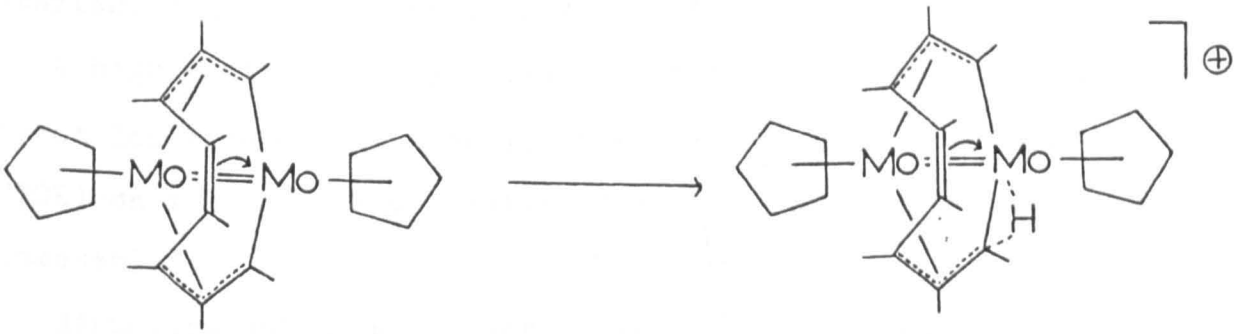
dropwise at -78°c to a yellow solution of (VI) in ether was reported to give the 1:1 adduct (VIII), $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ a colourless crystalline salt.[33]

The presence of a high field triplet at -2.6ppm in the ^1H n.m.r. of (VIII) together with a highly deshielded ^{13}C resonance at 346ppm indicated that protonation had taken place at the metal centre to yield a hydrido-alkylidyne complex. The hydride and carbyne ligands were thought to lie in a trans configuration due to the n.m.r. equivalence of the phosphite groups.

The spectroscopic data did not exclude an alternative structure in which the proton was involved in a 3 centre 2 electron interaction with both the metal and the α-carbon of the carbyne. (below)

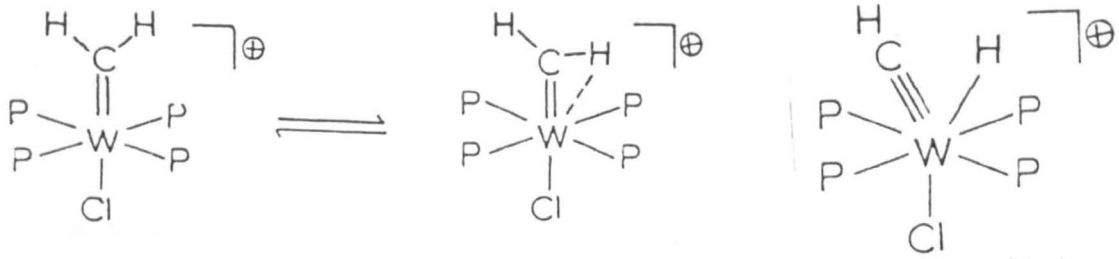


Precedent for this came from the protonation of the molybdenacyclononatetraene complex (70), which gave (71). X-ray analysis of the latter revealed that the proton was located between the molybdenum and an α-carbon.[105]



(70) (71)

Reaction of the methylidene complex (47) with $[CF_3SO_3H]$ gave the methylene complex $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$ (72). Variable temperature n.m.r. studies showed that the methylene ligand could adopt a distorted T-shaped geometry in which one of its hydrogens interacted with the formally 16 electron tungsten centre.[110]



(72)

(73)

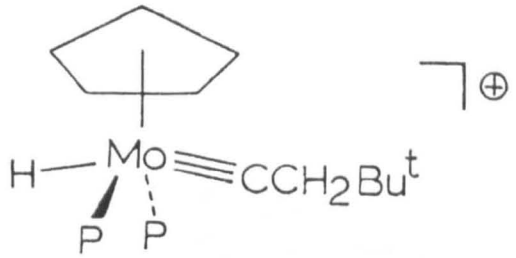
There is a delicate balance in this particular system; protonation by hydrochloric acid instead of by $[CF_3SO_3H]$ forms the hydrido-carbyne complex (73). Variation of the phosphine donor ligands may also affect the product type. The analogous $[W(CH)(dmpe)_2Cl]$ yielding a cationic hydrido-alkylidyne with either [HCl] or $[CF_3SO_3H]$.

In the light of these subsequent results the reaction of (VI) with $[HBF_4]$ was repeated in order to obtain crystals for an x-ray structure determination. This was accomplished by following the method of Bottrill[34] and recrystallising the crude product over several days from methylene chloride/hexane by layer diffusion at 0°c.

A high quality data set was required to improve the chances of direct location of the hydride. Data were collected at low temperature (250K) on a large x-ray crystal of roughly uniform dimensions (0.5mm diameter).

Structure solution and refinement progressed smoothly to a final R = 0.022. The results clearly support the original formulation of (VIII) as

a hydrido-alkylidyne complex. Views of the molecule are given in Figures 1.25 and 1.26.



(VIII)

A peak for the hydride ligand was found in one of the final difference maps (0.7 electron $Å^{-3}$) and refined to a reasonable geometry, the hydride located at 1.74(3)Å from the molybdenum in a position roughly bisecting the two trimethylphosphite ligands. The average H-Mo-P angle = 62.6(7)°. The hydride is trans to the alkylidyne moiety; H-Mo-C = 106.0(8)°.

The refined Mo-H distance compares favourably with those found for other terminal molybdenum-hydrides in well-determined x-ray structures and neutron diffraction studies.[110] (Table 1.6)

Structural comparisons between (VIII) and the parent complex (VI) also support the hydrido-alkylidyne formulation. The interligand angle between the phosphite ligands in (VIII) is much greater, 121.9(1)°, than that of 93.5(1)° found in (VI). This opening out is explained by the need to accomodate the hydride ligand. The Mo≡C triple bond in (VIII) shows no lengthening over that found in (VI) but is identical at 1.798(2)Å. Once again the carbyne unit is linear, Mo-C(7)-C(8) = 178°, further evidence that the $^{\alpha}$-carbon C(7) is not involved in an unusual interaction.

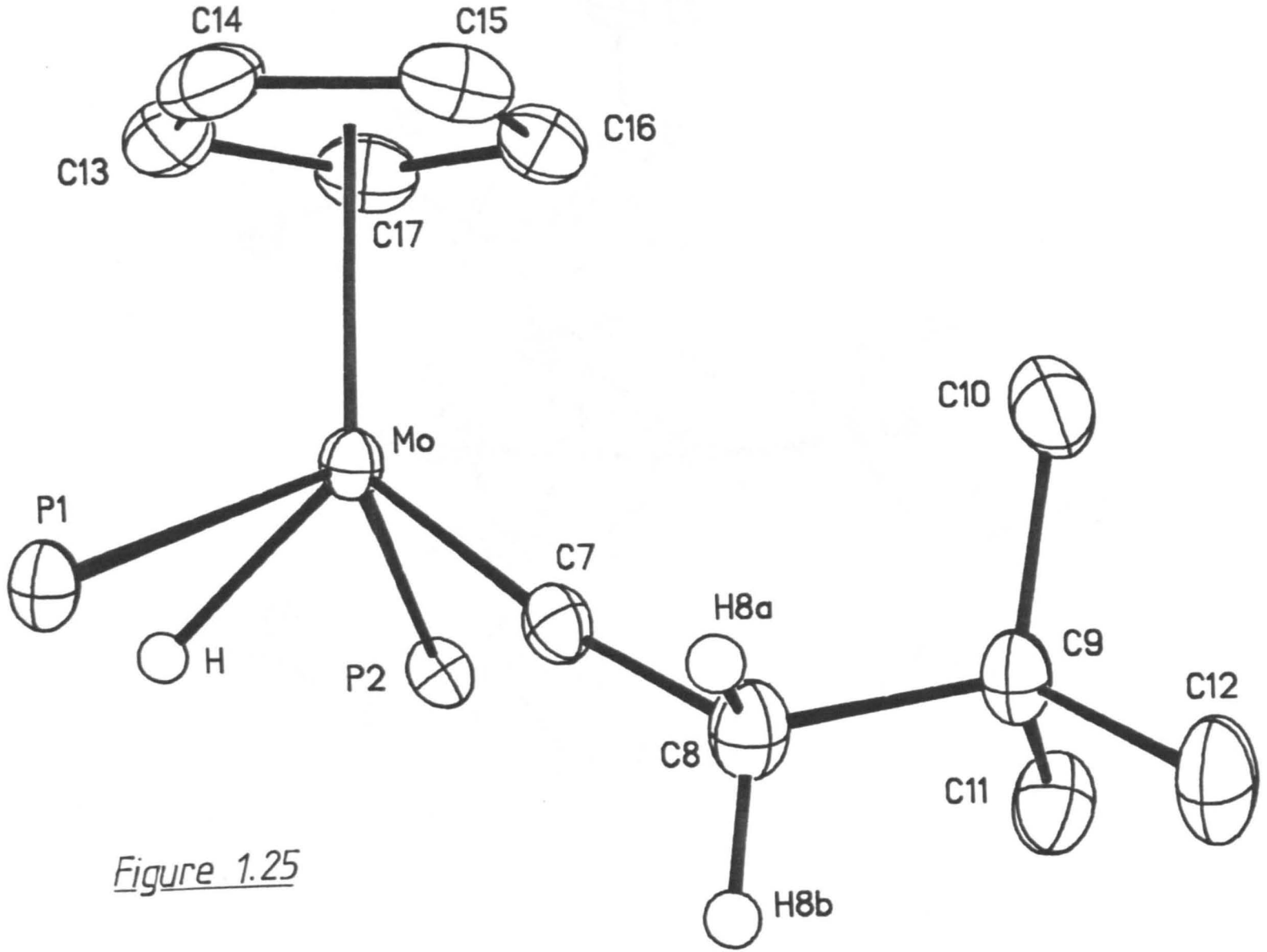


Figure 1.25

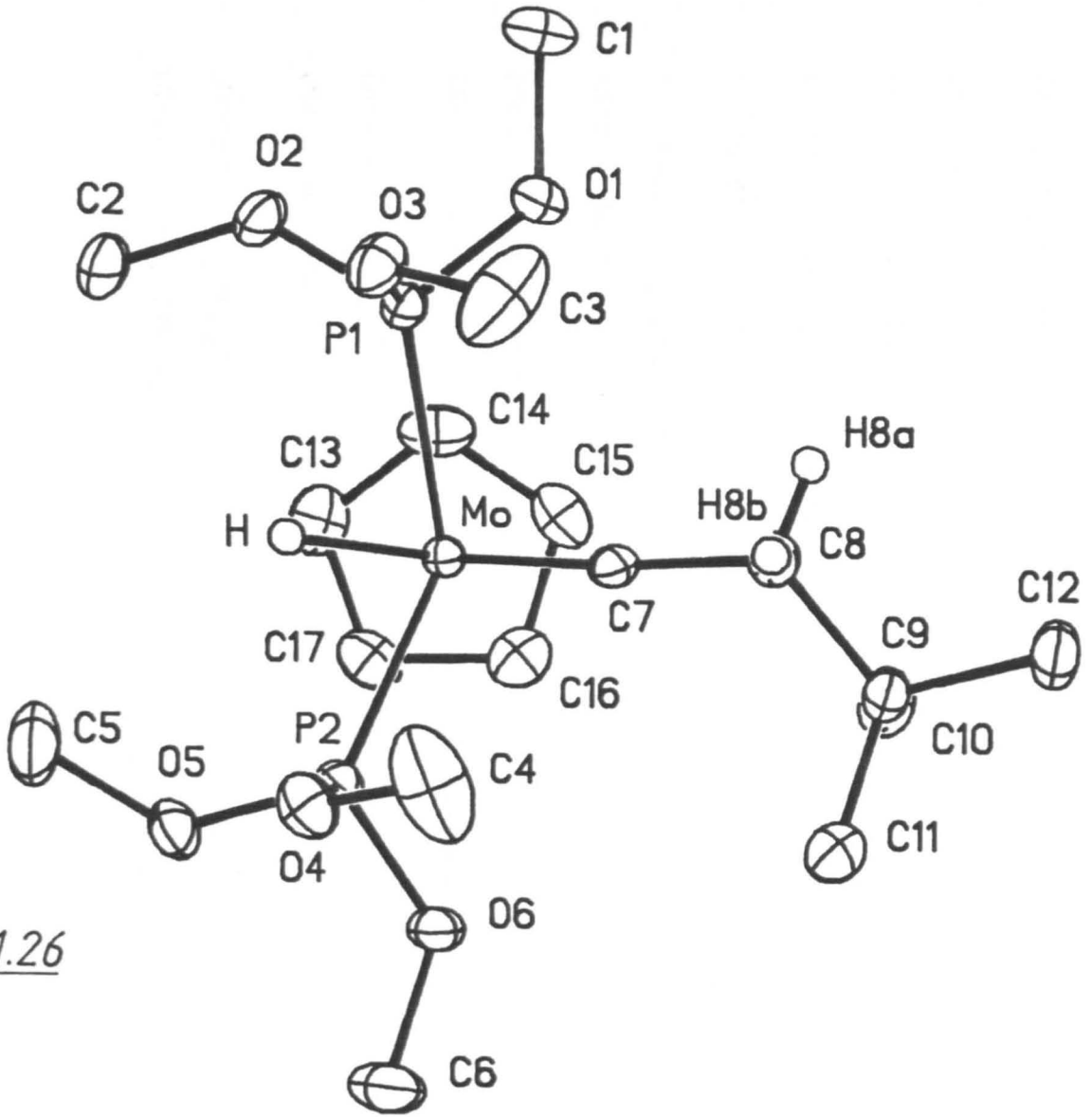

C1
O2
C2
O3
O1
C3
P1
C14
C13
C15
H8a
H8b
H
Mo
C8
C7
C12
C9
C17
C16
C5
P2
O5
C4
C10
O4
C11
O6
C6

Figure 1.26

TABLE 1.6

	Mo—H, Å	Ref.
$[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$-$[BF_4]$ (VIII) (X-ray data, 200 K)	1.74(3)	This work
$[Mo(PMe_3)_5(H)_2]$ (X-ray data, 295 K)	1.68(4) 1.67(3)	107
$[Mo(CO)'H)(\eta\text{-}C_5H_5)_2][Mo(CO)_3$-$(\eta\text{-}C_5H_5)]$ (X-ray data, 176 K)	1.76(8)	56i
$[Mo\{P(OMe)_3\}_4(H)(\eta^2\text{-}OCOCF_3)]$ (X-ray data, 298 K)	1.59(4)	108
$[Mo(PMe_3)_4(H)(BH_4)]$ (X-ray data, 298 K)	1.63 (unrefined)	109
$[Mo(H)_2(\eta\text{-}C_5H_5)_2]$ (Neutron data)	1.685(3)	110
$[Mo(PMePh_2)_4(H)_4]$ (X-ray data, 298 K)	1.66(13) 1.79(9) 1.70(10) 1.64(11)	111

The mean Mo-P distance of 2.390(1)Å is considerably longer than that observed for (VI) (2.329(1)Å). This is as expected; protonation of (VI) would reduce the electron density at the metal centre, lowering the amount of π-backbonding to the phosphites and lengthening the Mo-P bonds.

ii) Reaction with $[CF_3COOH]$

Whilst reinvestigating the protonation of (VI), its reaction with trifluoroacetic acid was studied. One equivalent of $[CF_3COOH]$ was added dropwise to a stirred solution of (VI) in diethylether at -78°c. On warming gradually to room temperature the colour of the solution changed from yellow to orange-red. Careful work-up of the product, (IX), gave a pale orange microcrystalline solid which was only slightly soluble in ether.

The ^1H n.m.r. of this product (CD_2Cl_2, room temp.) indicated the presence of cyclopentadienyl and trimethylphosphite protons, but there were no resonances attributable to the CH_2Bu^t moiety, indicating that cleavage of this fragment had taken place. There was however, a further signal, integrating for one proton, at 7.66ppm. This appeared as a triplet, presumably due to coupling to two equivalent phosphorus nuclei, with $J_{(P-H)}$ = 78Hz.

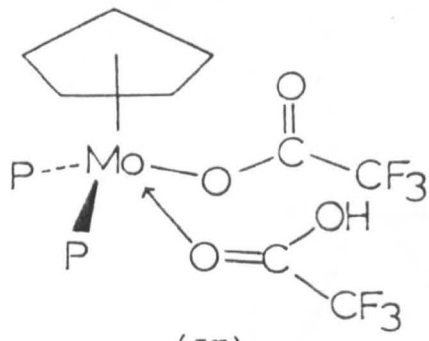
A parallel study on the reaction of (VI) with $[CF_3SO_3H]$,[51] seemed to give an analogous product to (IX), (74). This too no longer possessed a carbyne ligand and had an acidic proton at 8.94ppm (triplet, $J_{(P-H)}$ = 76Hz). The $^{13}C\{^1H\}$ n.m.r. of this, in addition to cyclopentadienyl and phosphite signals, showed a quartet at 119.4ppm ($^1J_{(C-F)}$ = 319Hz), attributable to the presence of CF_3SO_3 ligands, confirmed by the ^{19}F

n.m.r. spectrum which consisted of a singlet at -78ppm.

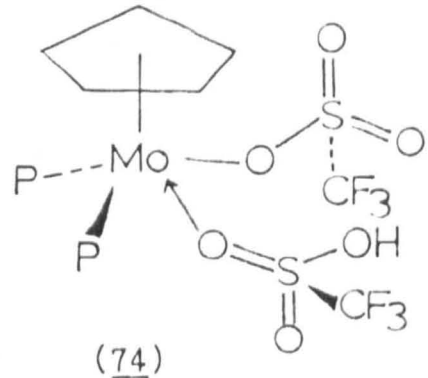
In order to determine the nature of these compounds a single crystal x-ray study was carried out on (IX). The small dimensions of the data crystal (0.3x0.1x0.08mm) were less than ideal but larger crystals of (IX) could not be obtained, and all attempts to crystallise (74) proved unsuccessful.

Although data were collected at low temperature, the structure refined to a final R of only 0.075. Problems were encountered with disorder of a CF_3CO_2 moiety.

On the basis of the x-ray results (IX) was formulated as $[Mo(\eta^1\text{-}OCOCF_3)(CF_3CO_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ as shown below with the analogue (74).



(IX)



(74)

The molecular geometry of (IX) is shown in its major (62%) and minor (38%) in Figures 1.27-1.29.

The molybdenum has a four legged pianostool geometry. In this complex the two $[P(OMe)_3]$ ligands are cisoid; P-Mo-P = 89.0(1)°. The other two sites are ocupied by two monodentate trifluoroacetate groups, one of which is disordered. The low accuracy of the structure and the problem of disorder meant that direct location of the acidic hydrogen, which had been observed in the n.m.r. and was required for neutrality of the complex, was not possible. The geometry of the disordered CF_3CO_2

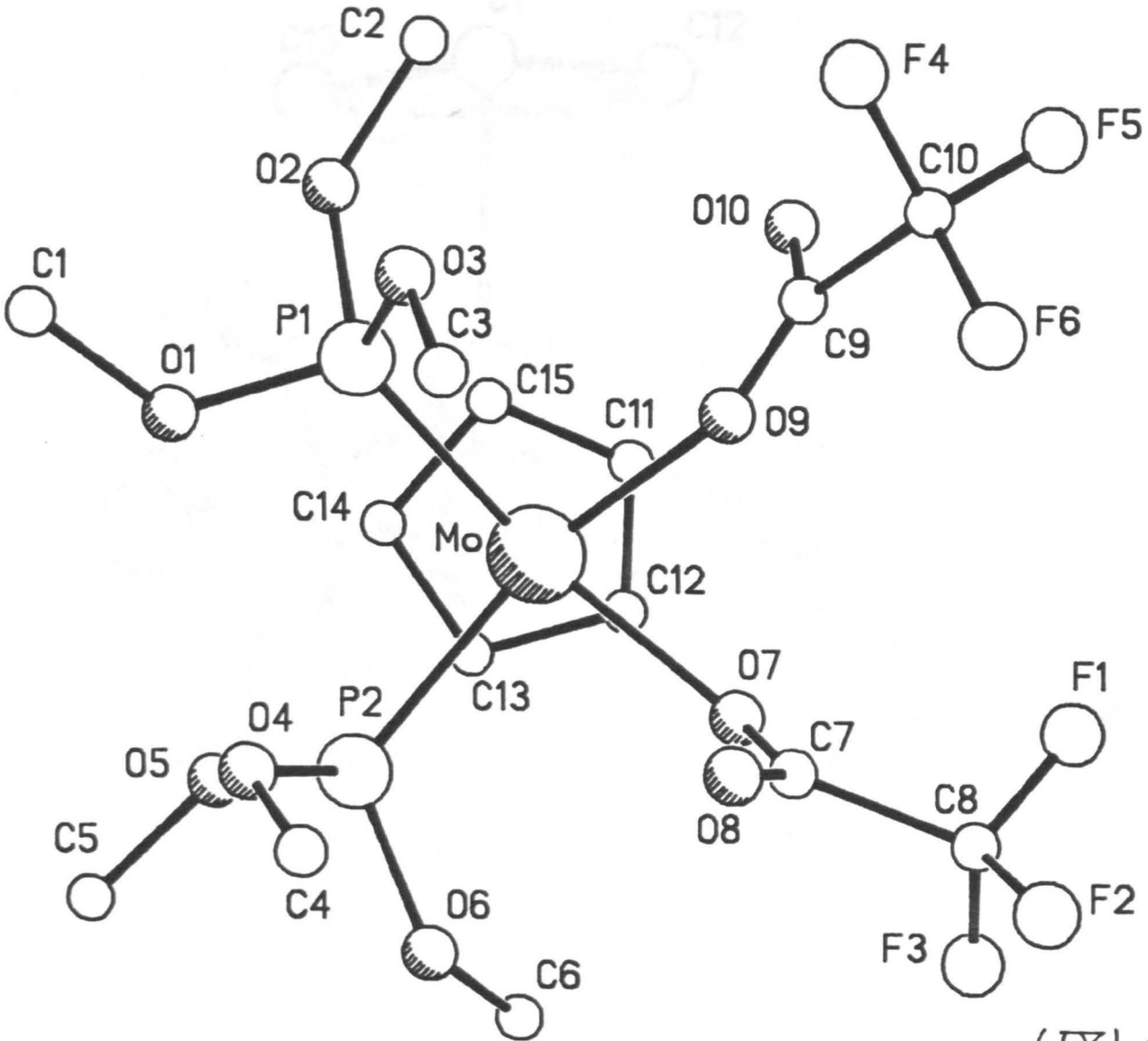


Figure 1.27

(IX) 68% Conformer

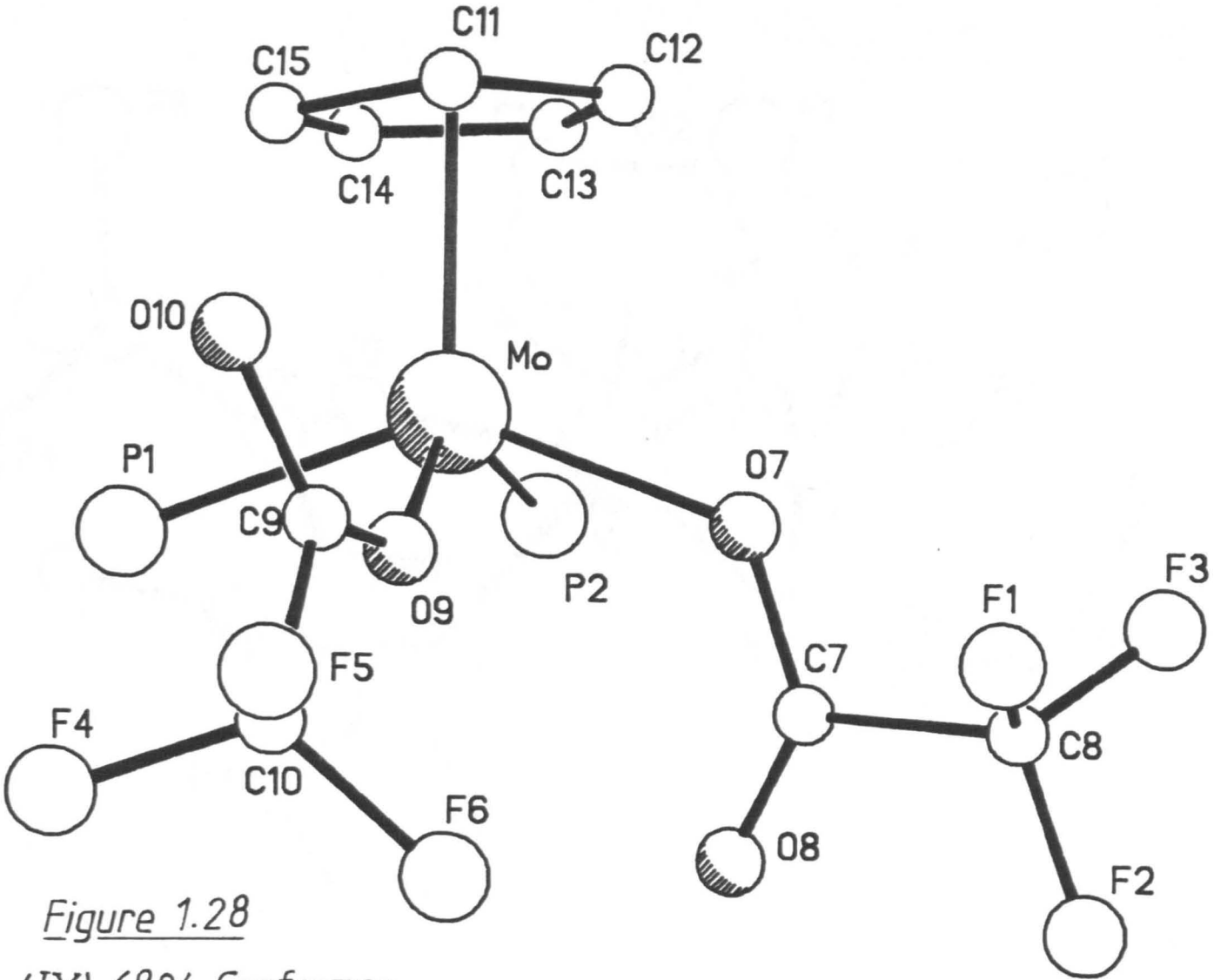


Figure 1.28

(IX) 68% Conformer

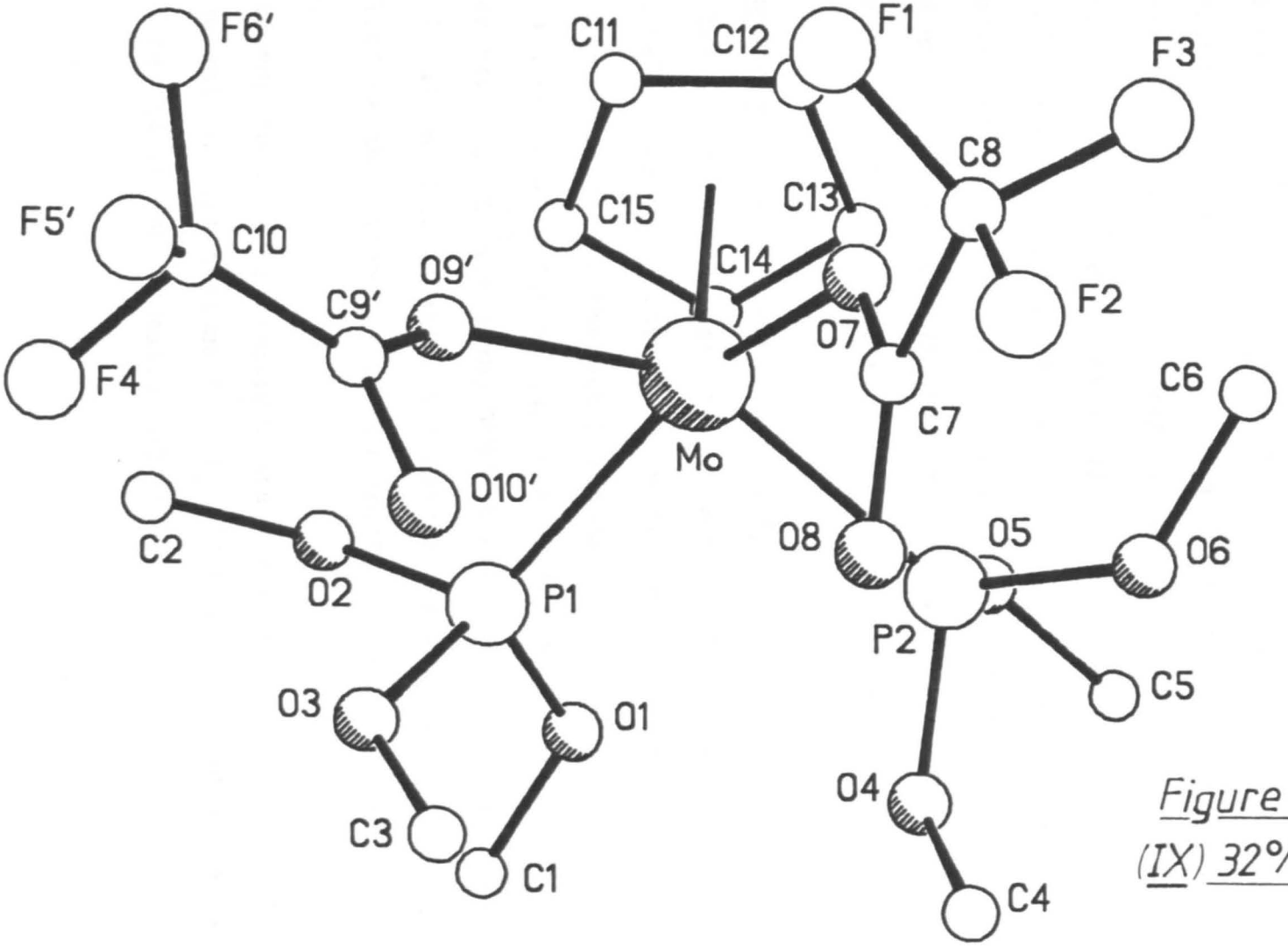


Figure 1.29

(IX) 32% Conformer

ligand did suggest that the hydrogen is associated with its uncoordinated oxygen (at least in the solid state).

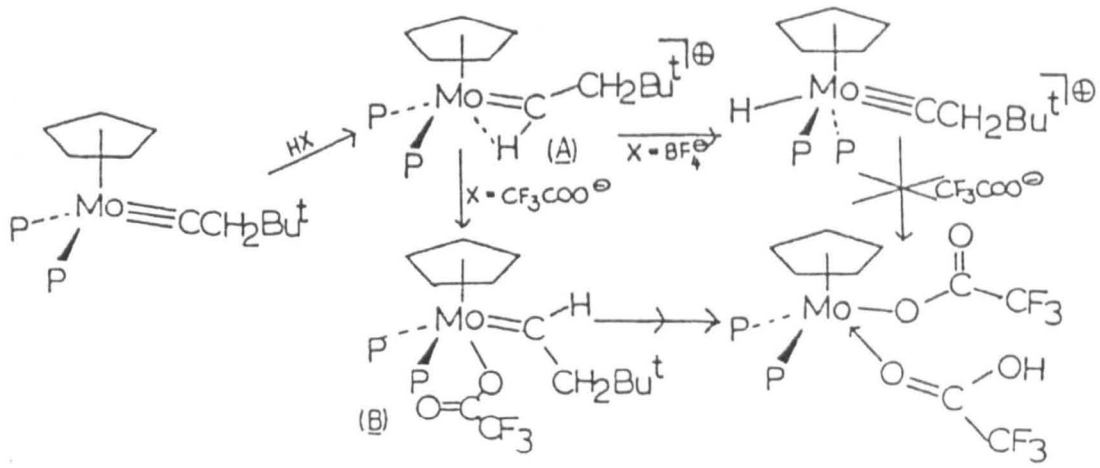
The acetate moiety which was unaffected by disorder had C-O bond lengths of 1.280(15)Å and 1.17(2)Å for the coordinated and uncoordinated oxygens respectively, these being due to C-O single and double bonds. In both orientations of the disordered acetate the longer C-O bond is associated with the uncoordinated oxygen. [C(9)-O(9) = 1.13(3)Å, C(9)-O(10) = 1.22(3)Å and C(9)'-O(9)' = 1.18(4)Å, C(9)'-O(10)' = 1.27(5)Å] The high esd's of these lengths make the assignment somewhat tenuous but in the absence of other intra- or inter-molecular hydrogen bonding contacts, the formulation of the ligand as a bound trifluoroacetic acid molecule is the best available explanation.

Mechanism of the Protonation of (IX)

If the assumption is made that reaction of (VI) with either [HBF_4] or [CF_3COOH] proceeds initially by attack of a proton, then two sites of attack may be proposed, the metal centre and the alkylidyne carbon.

If attack is directed at the former, the reaction may be regarded as frontier controlled,[112] since the HOMO of (VI) is localised largely on the metal. If at the latter site, the reaction may be described as charge controlled as the carbon is at the negative end of the strong Mo≡C dipole.

Evidence that these reactions are charge controlled was provided by the observation that treatment of (VIII) with trifluoroacetic acid did not result in the formation of (IX).

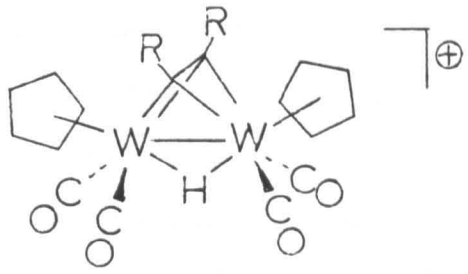


Scheme 1.9 Protonation of (VI)

It is therefore proposed that initial attack occurs at the alkylidyne carbon yielding a formally '16 electron' alkylidene intermediate (A), stabilised by a C-H-Mo three centre interaction. In the absence of a coordinating anion this rearranges to the more thermodynamically stable hydrido-alkylidyne isomer which is resistant to attack by trifluoroacetate. The intermediate (A) is however rapidly attacked by coordinating anions such as $[CF_3COO]^-$ or $[CF_3SO_3]^-$, giving (B) in the case of trifuoroacetate. This may then be subject to further protonation at the carbene carbon, followed by elimination of the six carbon fragment, (probably as either 3,3-dimethylbut-1-ene or 2,2-dimethylbutane).

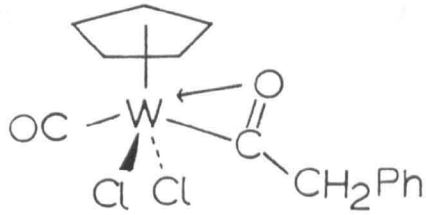
This is the first reported protolytic cleavage of a metal-carbon triple bond. The benzylidyne complex $[Re(CO)_2(CPh)(\eta\text{-}C_5H_5)][BCl_4]$ has been reduced via the carbene species $[Re(CO)_2(CHPh)(\eta\text{-}C_5H_5)]$ to a benzyl complex $[HRe(CO)_2(CH_2Ph)(\eta\text{-}C_5H_5)]$ by $[AlHEt_2]$.[113] Fischer et al have observed cleavage of the carbene fragment in $[W(CO)_5\{C(OMe)Ph\}]$ upon treatment with [HX], (X = Cl,Br,I), the product being $[HW(CO)_5X]$.[113]

Protonation of carbyne complexes continues to give interesting results. Reaction of the tungsten carbyne $[W(CO)_2(CC_6H_4Me)(\eta\text{-}C_5H_5)]$ with $[HBF_4]$ yields (75) in which two carbyne moieties have coupled to produce an acetylene ligand.[114]

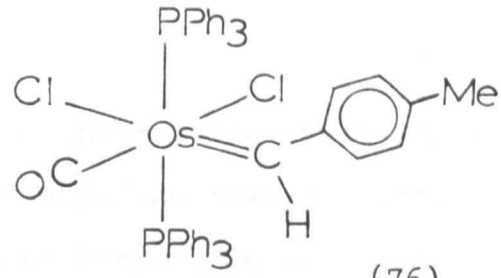


(75)

Alternatively treatment of the analogous benzylidyne species with two equvalents of [HCl] yields the η^2-acyl complex below.[115]



Reaction of Roper's osmium carbyne with [HCl] gave a neutral carbene complex (76).



(76)

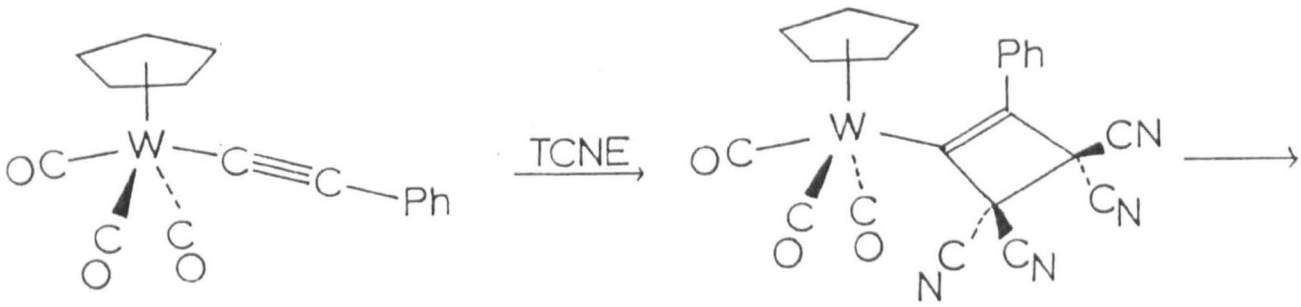
Reaction of $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

with Carbon Electrophiles

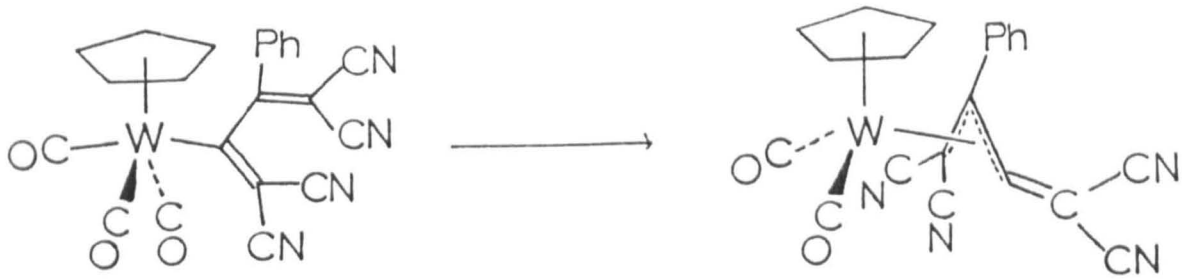
i) Tetracyanoethylene

In further exploring the chemistry of (VI) with electrophilic reagents its reaction with tetracyanoethylene (TCNE) was investigated.

It was anticipated that the reaction might proceed with C-C bond formation leading to a metallacyclobutene complex. This was based partly on the observations of Bruce et al that addition of TCNE to the acetylide complex $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ afforded the structurally characterised cyclobutenyl complex (77).[116]



(77)

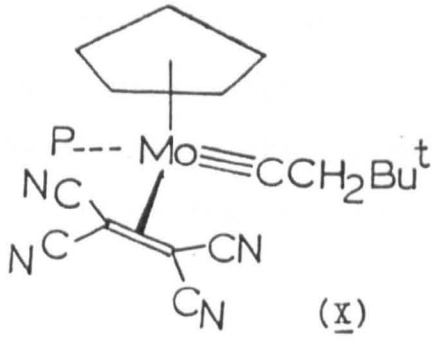


This compound has an interesting chemistry involving ring opening reactions to give butadienyl and π-allyl complexes. The structures of these being determined by comparison with ruthenium analogues for which x-ray determinations were carried out.[117,118]

Addition of one equivalent of TCNE to a stirred methylene chloride solution of (VI) at room temperature resulted in a rapid colour change from yellow to deep green. A green solid was isolated after column chromatography of the solution on alumina. This was observed to change colour over a period of one day in the solid state, or less than one hour in [CH_2Cl_2] solution to a very pale pink.

There was no noticeable difference between the infra red spectra of the green and pink solutions. The major feature was a broad band at 2220cm^{-1} indicative of a ν(C=N) stretching frequency. The n.m.r data were also essentailly identical for the green or pink material. These indicated the presence of the cyclopentadienyl group, one trimethylphosphite ligand and retention of the alkylidyne moiety. The carbyne carbon appeared as a doublet at 330ppm in the ^{13}C n.m.r. spectrum. Three weak resonances between 125 and 120ppm were attributed to carbons of a TCNE ligand.

Attempted crystallisations of either the green or pink solutions by CH_2Cl_2/hexane layer diffusion at 0°c resulted in the formation of colourless prisms. One of these was mounted under nitrogen and a crystal structure determination carried out on the material, (X). This was solved and refined to a final R = 0.036. Compound (X) was found to be the mono-TCNE substituted derivative of (VI).



(X)

The molecular geometry is shown in Figures 1.30-1.32. The carbyne unit is similar to that found in the parent compound Mo=C(3) = 1.771(3)Å and the Mo-C(3)-C(4) angle is 177.3(4)°.

The lone phosphite ligand showed disorder in two of the three methoxy groups. For these two arms of the ligand two positions were refined for the oxygen atoms although only one position was discernable for the methyl carbon. This particular phenomenon has been seen before in trimethylphosphite complexes, e.g. in $[Mo(CO)_2(\eta^1\text{-}C(Me)NPh)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$,[65] $[Mo\{CC(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)Cl]$[119] and compound (IV). The resulting bond lengths and angles within the phosphite ligand are less reliable than usual. The Mo-P bond of 2.430(2)Å is one of the longest found in the series of compounds (I) through (X). This no doubt reflects the exceptional π-acceptor capability of the TCNE ligand.

This property is also reflected by the long C(1)-C(2) bond of 1.503(7)Å between the central carbons of the TCNE itself. This together with the fairly short Mo-C(1) and Mo-C(2) contacts of 2.245(5)Å and 2.209(5)Å indicates a strong π-interaction between the metal and the $[C_2(CN)_4]$ ligand.

The C(1)-C(2) vector has a skew orientation w.r.t. the $(\eta\text{-}C_5H_5)$ plane, similar to the acetylene ligand in (I). The C(1)-C(2)-Mo-P torsion angle is close to zero.(7.3)

The planarity of the TCNE ligand is lost on coordination to the metal, the four cyano substituents all being bent away from the molybdenum. The angle between the planes C(11)-C(1)-C(12) and C(23)-C(2)-C(24), representing the two different halves of the ligand is 74.1°.

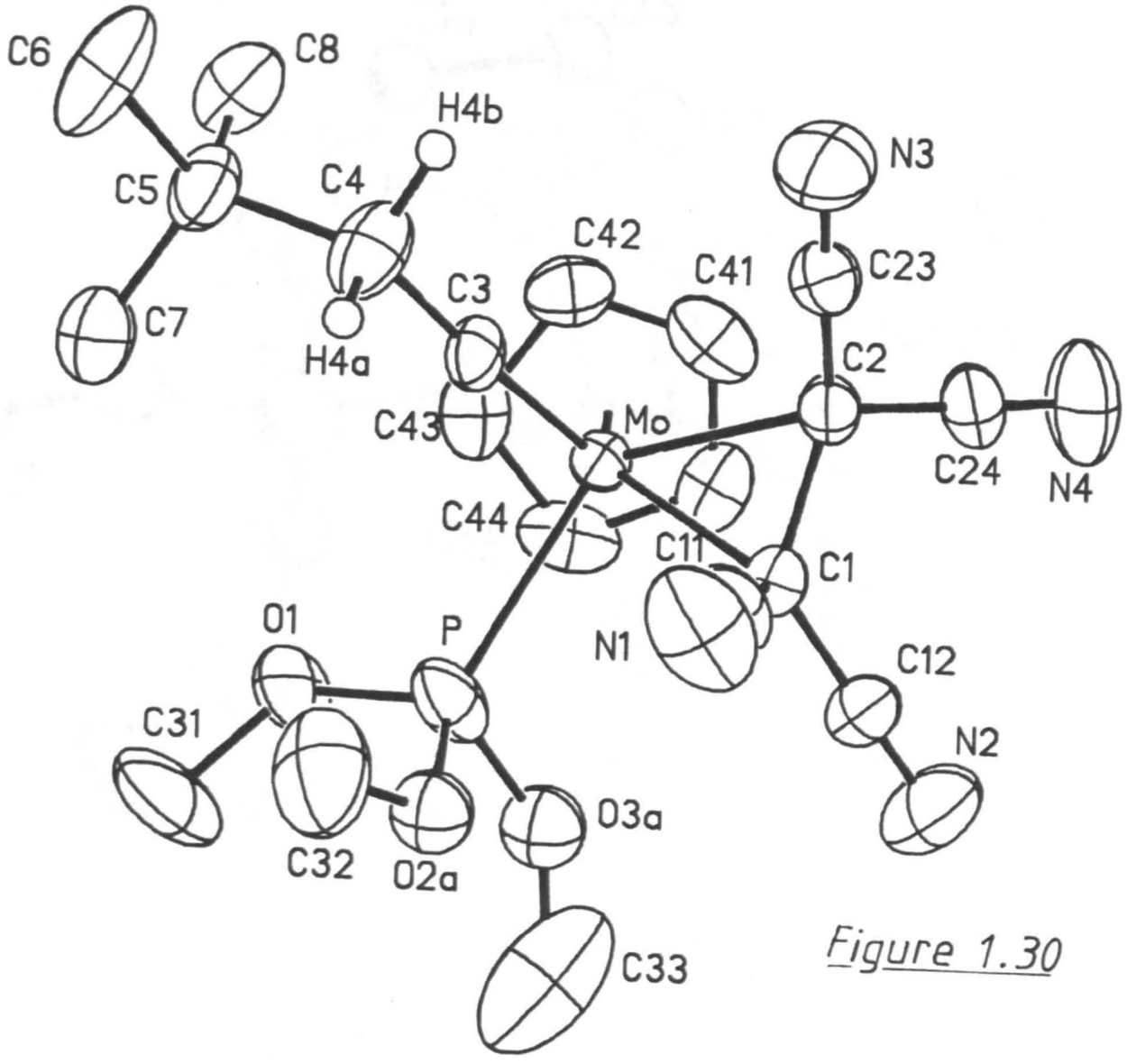

C6
C8
H4b
C5
C4
N3
C42
C41
C23
C3
C7
H4a
C2
C43
Mo
C24
N4
C44
C11
C1
O1
P
N1
C12
C31
N2
O3a
C32
O2a
C33

Figure 1.30

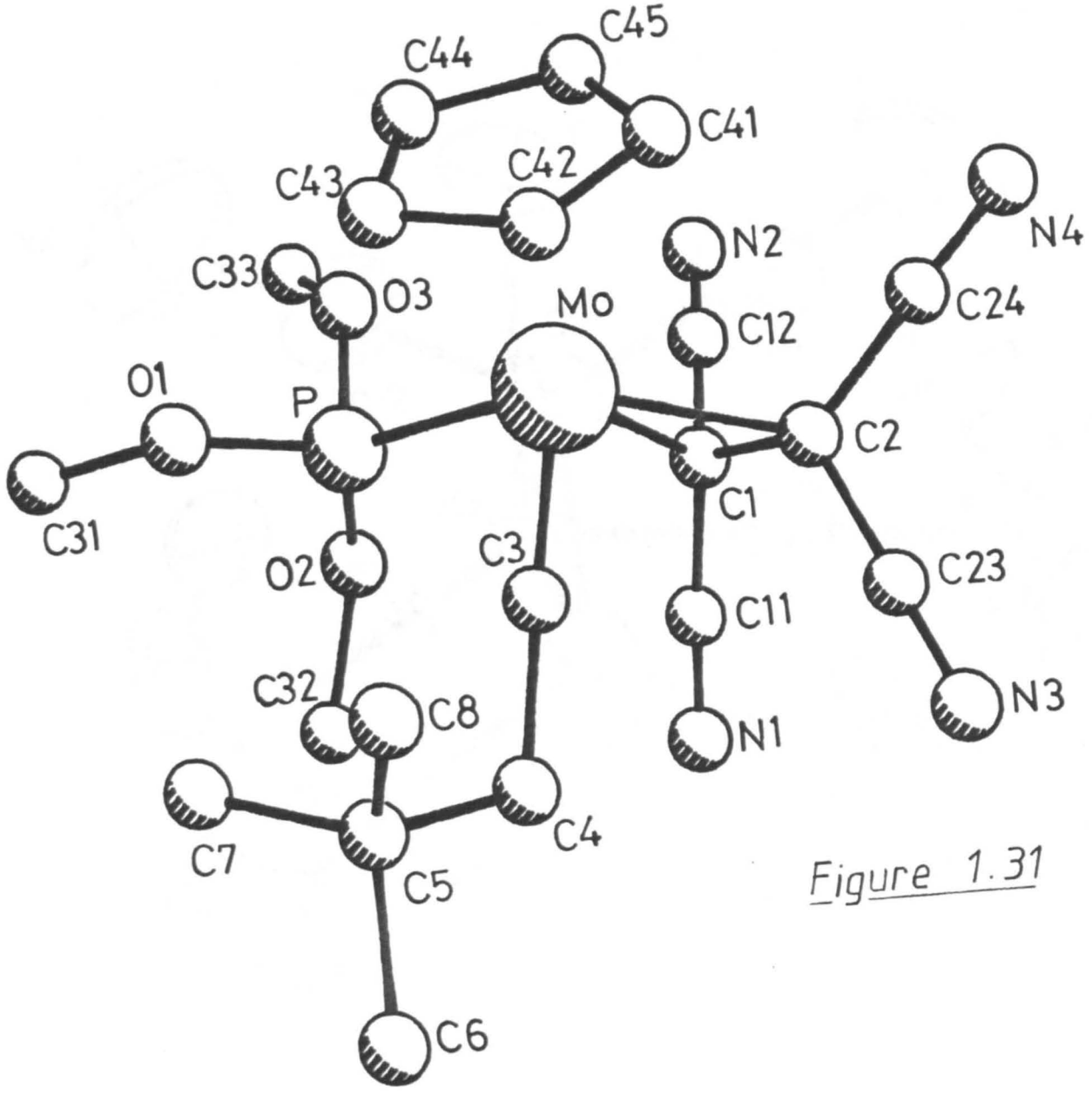

C45
C44
C41
C42
C43
N2
N4
C33
O3
Mo
C12
C24
O1
P
C2
C31
C1
O2
C3
C23
C11
C32
C8
N3
N1
C7
C4
C5
C6

Figure 1.31

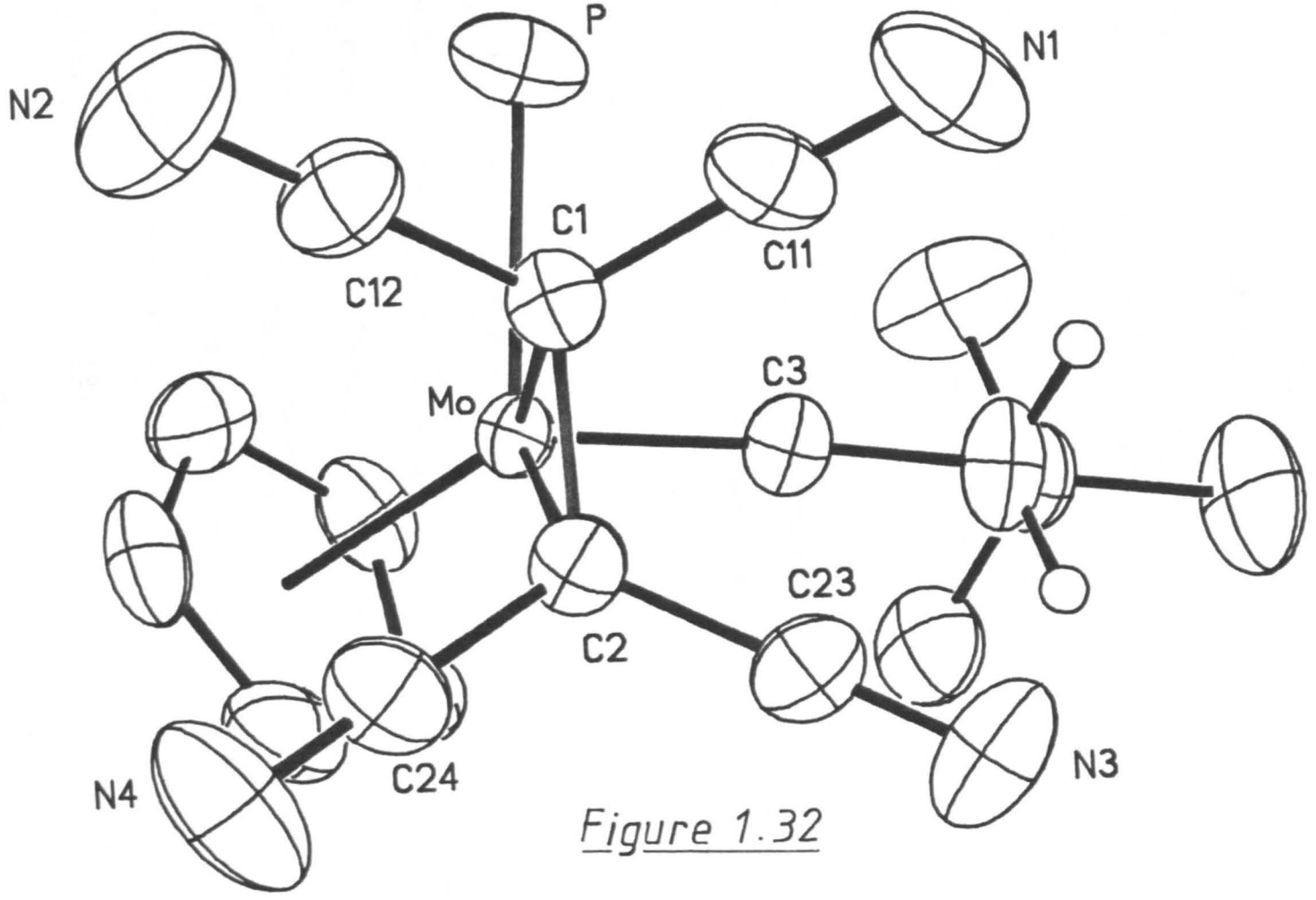


Figure 1.32

Interestingly the C-C(N) bond distances are considerably shorter than C(1)-C(2), ranging from 1.425 to 1.445(8)Å. The C-N bonds lie between 1.121 and 1.156(7)A, indicating a high bond order.

The angles about the molybdenum for the three ligands of the 'base' of the pianostool reflect the larger bite of the η^2-coordinate TCNE; P-Mo-C' = 100.9(1)°, P-Mo-C(3) = 88.8(2)° and C'-Mo-C(3) = 95.5(2)°, where C' is the midpoint of the C(1)-C(2) bond.

The cyclopentadienyl carbons are at distances from the metal ranging from 2.335 to 2.439(6)Å, with the two closest carbons lying over the Mo=C alkylidyne bond.

It is interesting to compare the ^{13}C chemical shift of the carbyne carbon in (X) with that of (VI) and other analogous complexes. (Table 1.7).

Compound	$\delta(^{13}C)$ ppm	
$[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (VI)	299.8	(Ref. 34)
$[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (VIII)	346.7	(Ref. 34)
$[Mo\{\eta^2\text{-}C_2(CN)_4\}(CCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (X)	338.9	This work
$[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_3\{COH(CF_3)_2\}_2)]$ (XI)	311.6	This work
$[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I][BF_4]$ (XIII)	392.6	This work
$[Mo(CO)(CCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (57)	316.3	(Ref. 51)
$[Mo(CO)_2(CCH_2Bu^t)(\eta\text{-}C_5H_5)]$ (58)	332.8	(Ref. 51)

Table 1.7.

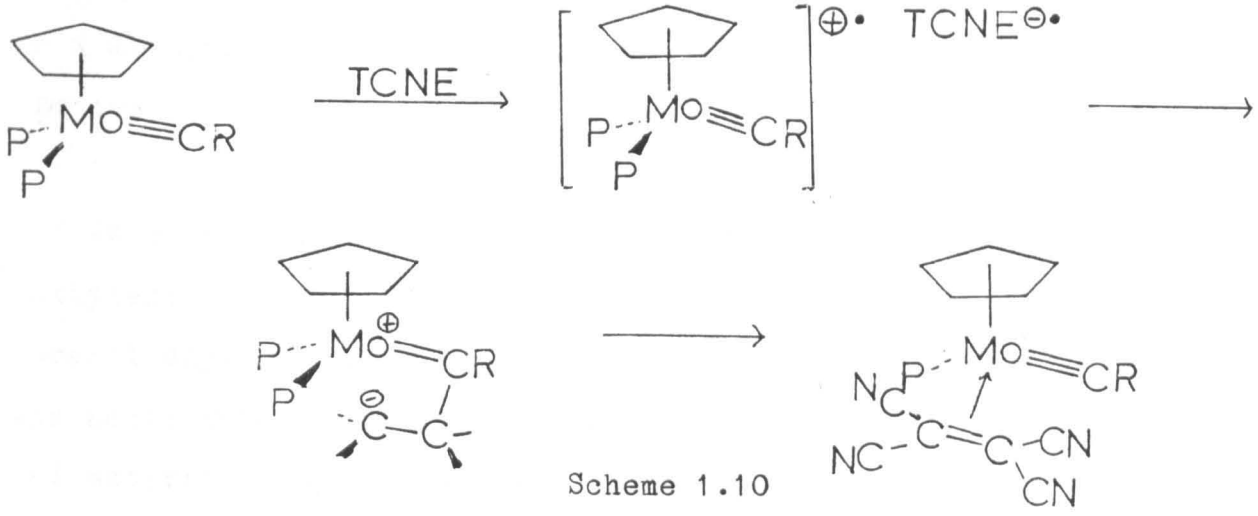
N.m.r. Chemical Shifts for Molybdenum Alkylidyne Complexes

There seems to be a definite correlation between the shift of the carbyne carbon and the electron richness of the metal centre, influenced by the π-accepting capabilities of the other ligands. Consecutive replacement of $[P(OMe)_3]$ by CO in the complexes (VI) through (36) results in a stepwise deshielding of the α-carbon resonance. Replacement of $[P(OMe)_3]$ by the super π-acceptor TCNE deshields the carbon still further, and protonation of (VI) to give (VIII) has the dramatic effect of shifting the carbyne resonance downfield by close to 50ppm. These shifts may be compared to other ^{13}C resonances for carbyne carbons.[120-1]

Mechanism of Formation of (X)

The mechanism of the substitution of $[P(OMe)_3]$ by TCNE in the conversion of (VI) to (X) is uncertain. It seems likely though that the highly coloured green species is a reaction intermediate. Characterisation of this is yet awaited. Bruce et al. also observed intensely coloured intermediates during the formation of the cyclobutenyl complex (77). These were found to be paramagnetic. Davison and Solar[122] reported similar findings; addition of TCNE to $[Fe(CO)L(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$, L = CO, PPh_3 resulted in the formation of a deep green solution, the colour of which faded over a period of 1 hr. The intense colour was attributed to a charge transfer complex.

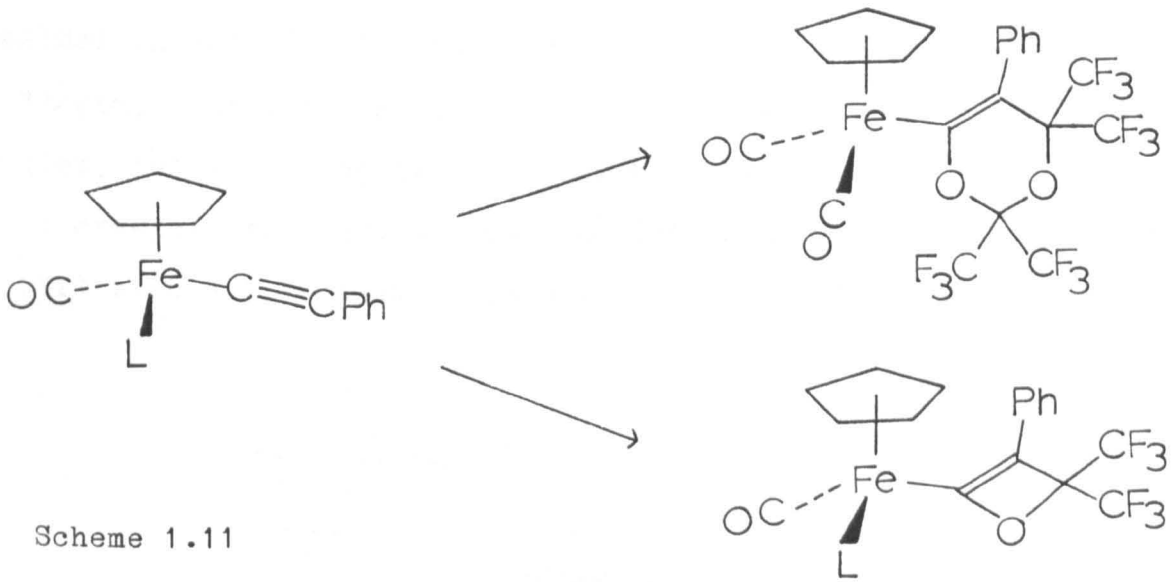
Assuming that the reaction of (VI) with TCNE does not proceed via a dissociative process, with initial loss of $[P(OMe)_3]$ a possible mechanism for the formation of (X) is given in Scheme 1.10. The involvement of radical species has not been investigated by e.s.r. studies, there is electrochemical evidence however that (VI) may undergo a facile one electron oxidation.[123]



Scheme 1.10

ii) Hexafluoroacetone

Davison and Solar have also investigated the reaction of the iron acetylide complexes [Fe(CO)L(C≡CPh)(η-C_5H_5)] with hexafluoroacetone, [$(CF_3)_2C$=O], the results of which are sumarised in Scheme 1.11.[124]



Scheme 1.11

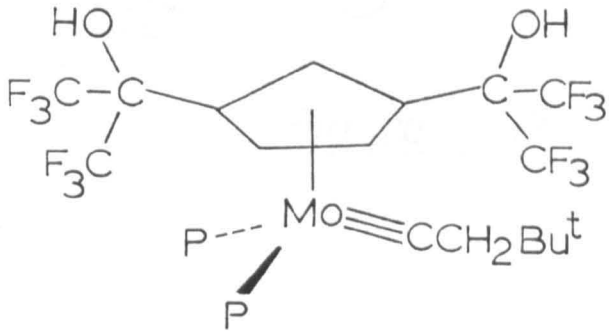
Adducts are formed involving 1 or 2 equivalents of hexafluoroacetone per iron. The 1:1 adducts are found to be stable with respect to further

ring expansion, evidence that the 2:1 adduct results from attack of HFA on a dipolar intermediate which collapses irreversibly to the 1:1 species.

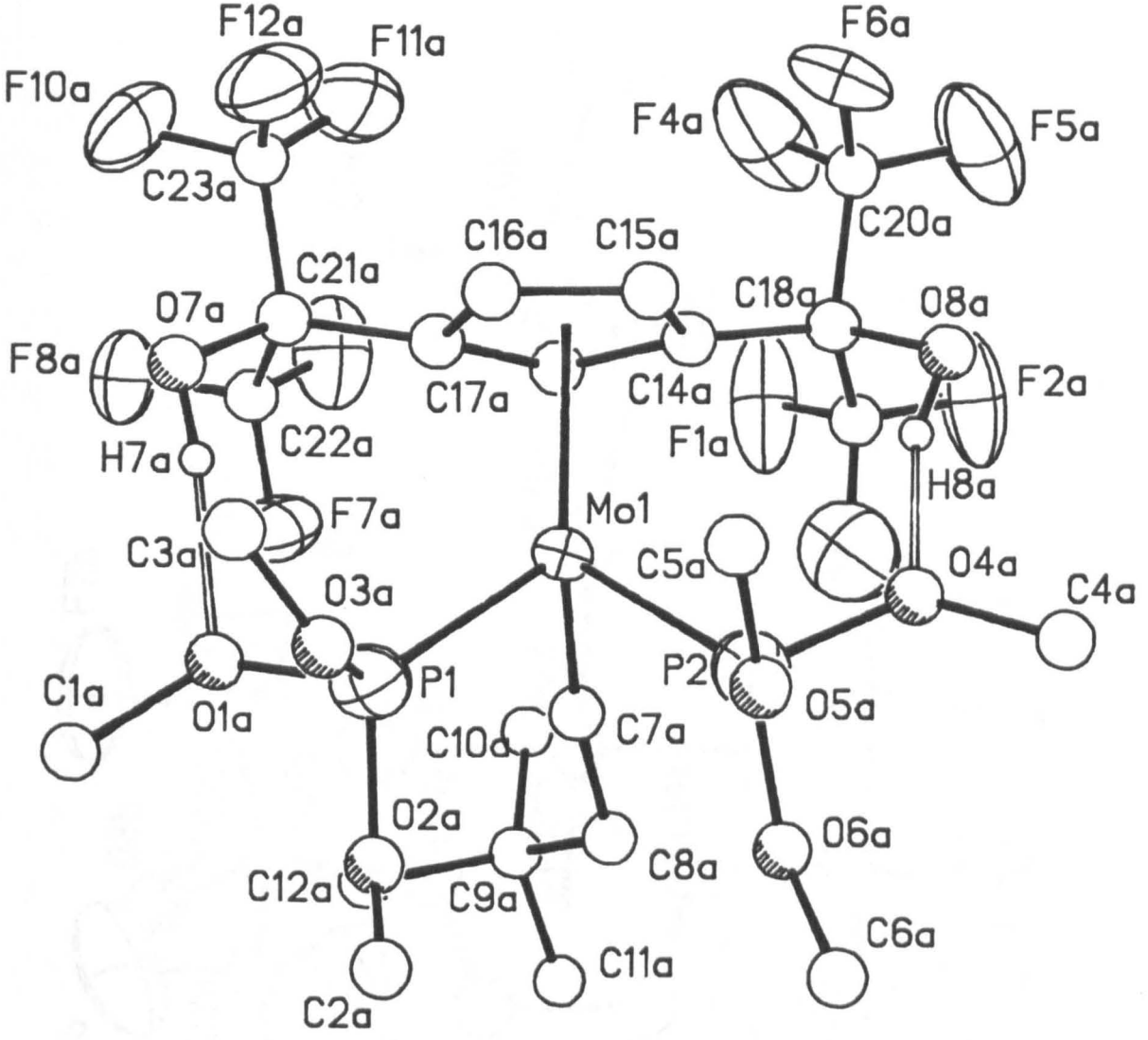
An excess of HFA was condensed into a Young's tube containing a methylene chloride solution of (VI). This was allowed to react for several days at 0°c. A slight colour change from yellow to pale orange was noticeable. Upon column chromatography this was found to be due to a red material (approx. 5% yield, ether fraction) of which there was insufficient to allow characterisation. The major fraction (60% yield, 1:1 ether/ hexane) was a yellow crystalline material (XI).

The ^{1}H n.m.r. was similar to that of (VI) except that the single resonance for the cyclopentadienyl protons had been replaced by signals integrating for 1 and 2 protons at 6·1ppm and 5·6ppm respectively. The signals for the carbyne ligand indicated that this functionality had remained intact. The $^{13}C\{^{1}H\}$ n.m.r. spectrum showed a low field triplet at 312ppm, attributable to the carbyne carbon. The ^{31}P n.m.r. was a singlet, due to two equivalent phosphite groups.

A crystal structure analysis of (XI) showed this to be a derivative of (VI) with a 1,3-disubstituted cyclopentadienyl ring.



(XI)


F12a
F11a
F10a
C23a
F6a
F4a
F5a
C20a
C16a
C15a
C21a
C18a
O7a
O8a
F8a
C17a
C14a
F2a
C22a
F1a
H7a
H8a
F7a
Mo1
C3a
C5a
O4a
C4a
O3a
P1
P2
C1a
O1a
O5a
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C9a
C6a
C11a
C2a

Figure 1.33

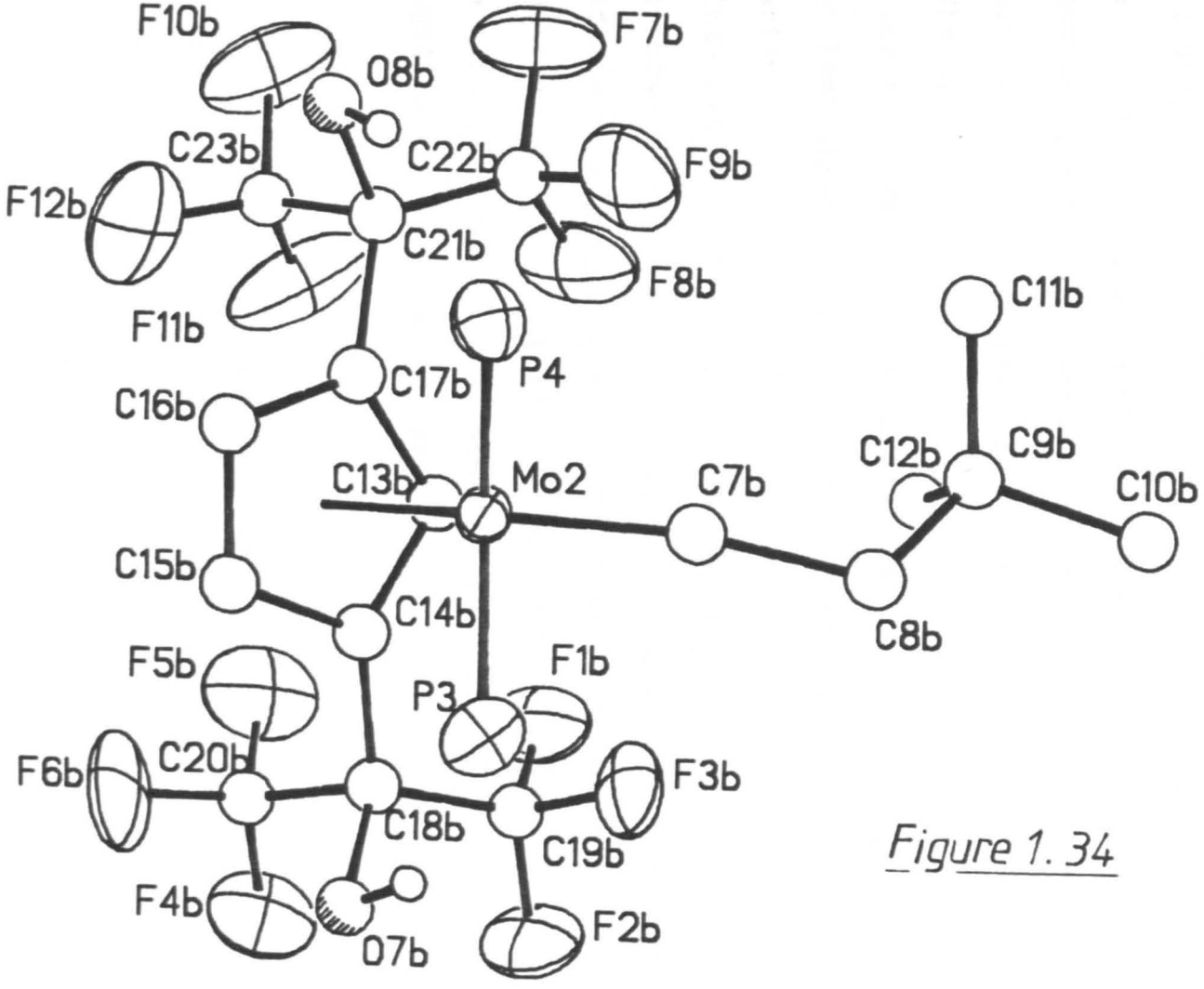

F10b
F7b
O8b
C23b
C22b
F9b
F12b
C21b
F8b
F11b
C11b
C17b
P4
C16b
C12b
C9b
C13b
Mo2
C7b
C10b
C15b
C14b
C8b
F5b
F1b
P3
C20b
F6b
F3b
C18b
C19b
F4b
O7b
F2b

Figure 1. 34

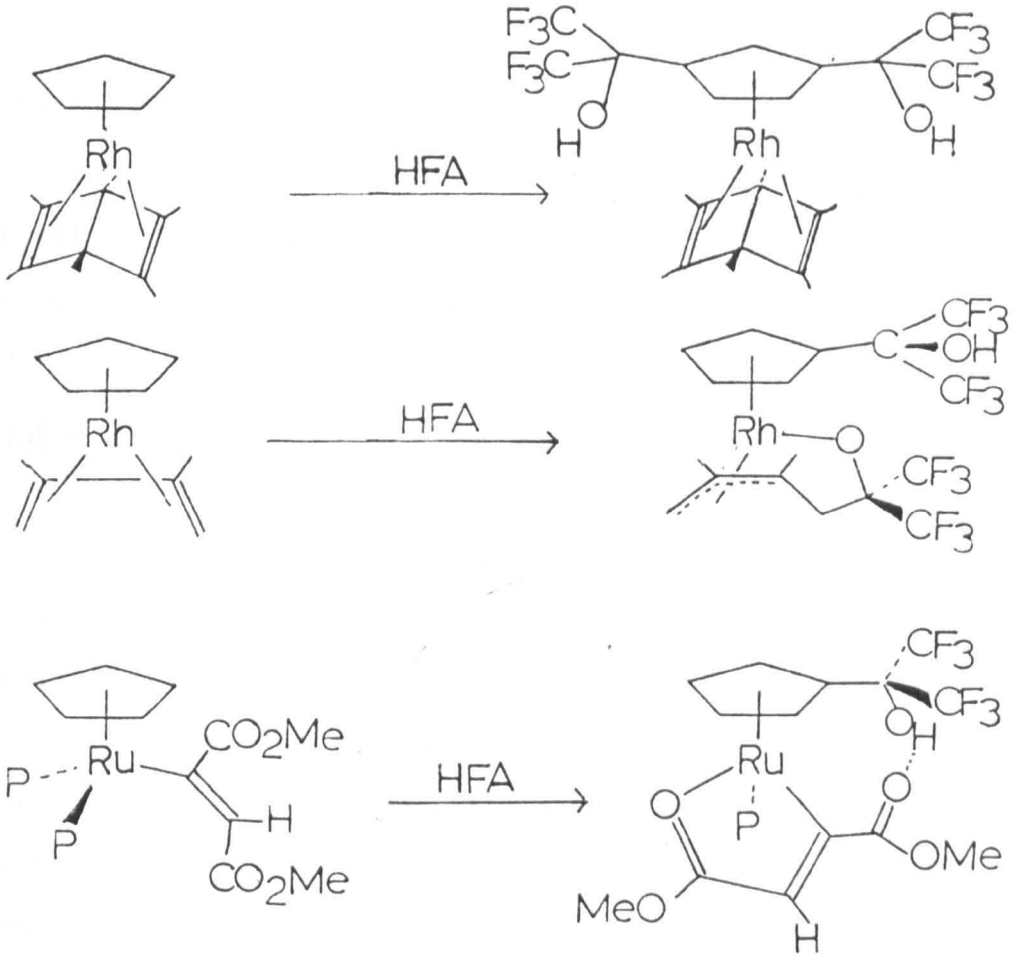
The substituted carbons possess hydroxyhexafluoropropyl groups which are the result of the formal insertion of a HFA molecule into the cyclopentadienyl C-H bond. The molecular geometry of (XI) is shown in Figures 1.33 and 1.34. Two crystallographically independent molecules were found. Short intramolecular contacts were seen betweenthe oxygen atoms of the ring substituents and two of the phosphite oxygens, indicative of hydrogen bonding between these centres (the mean O-O contacts for these interactions were 2.85Å).

The average Mo≡C bond distance is 1.783(8)Å which is comparable to that for the alkylidyne functionalities in (VI), (VIII) and (X). The Mo≡C-C bond angles average 171.5(7)°, showing more deviation from linearity than usual.

Interest in the structure also centres on the substituted cyclopentadienyl rings. The carbons bearing these groups lie slightly out of the ring planes, (av. = 0.1Å) towards the molybdenum. The C-OH bonds aree single (1.404(11)Å average) and the C-F bonds fall in the range 1.29 to 1.35(2)Å. The mean Mo-P bond length is 2.342(3)Å, longer by 0.01Å than that found in (VI).

Mechanism of the Formation of (XI)

Insetion of HFA into the C-H bonds of a cyclopentadienyl ligand has been observed previously in rhodium and ruthenium chemistry.[124-126]



P = PPh_3

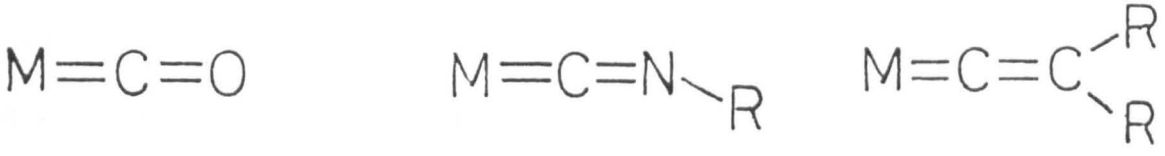
It is not known whether attack occurs directly at the Cp ring or if the insertion results via a more complex pathway in which the metal plays a role.

Section 1.4

The Formation and Chemistry of some Molybdenum Vinylidene Complexes

Introduction

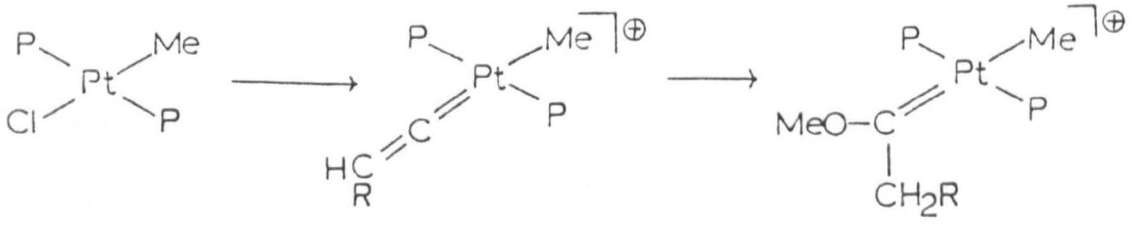
Whereas transition metal carbonyl and isocyanide chemistry has been extensively explored complexes with the isoelectronic vinylidene ligand remain relatively scarce and were unknown before 1973.



Carbonyl Isocyanide Vinylidene

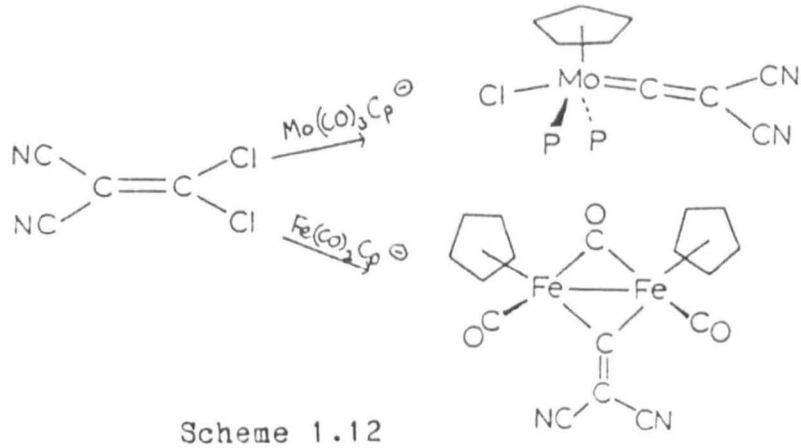
One reason for this is that uncoordinated vinylidenes themselves are highly unstable species.[127] All preparations of vinylidene complexes to date have been via modification of other unsaturated carbon ligands.

Chisholm and Clark proposed vinylidene intermediates in the reaction of the Pt complex (78) with $[Ag]^+$ in the presence of acetylenes.[128] Methanolysis of the intermediates to yield (79) was thought to occur.



(78) (79)

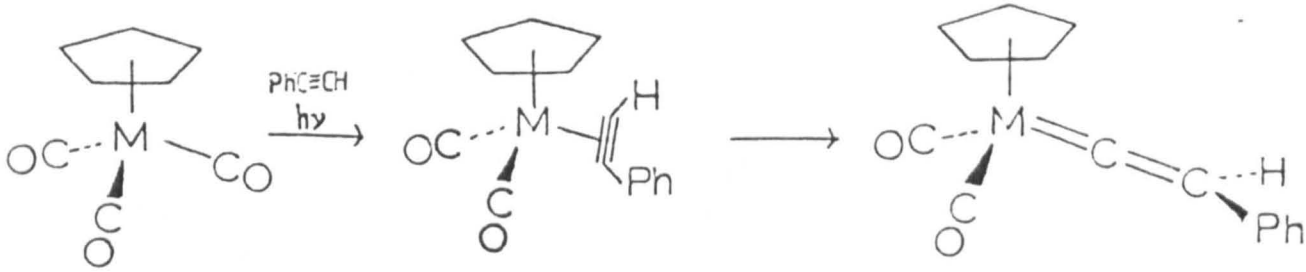
King and Saran synthesised both mononuclear and bridging dinuclear dicyanovinylidene complexes by reacting 1,1-dichloro-2,2-dicyanoethylene with anionic transition metal species.[129] (Scheme 1.12).



Scheme 1.12

Structural characterisations were carried out on two of these, (80)[119] and (81).[130] The dicyanovinylidene ligand was postulated as one of the strongest π-acceptor ligands known.

In 1977 Kolobova et al reported the formation of vinylidene complexes of the group VII metals on attempted photolytic replacement of CO by phenylacetylene.[131-133]



Once again rearrangement of a terminal alkyne to a vinylidene seems to be involved. Similarly $[Fe(C{=}CHPh)(depe)_2Cl]$ is formed upon addition of $[PhC{\equiv}CH]$ to $[Fe(depe)_2Cl_2]$,[134] and Beck et al have argued that the same type of isomerisation occurs for the four electron donor alkyne complex $[Mo(CO)(PhC{\equiv}CH)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ in giving the unstable 16 electron vinylidene species $[Mo(CO)(C{=}CHPh)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$.[135]

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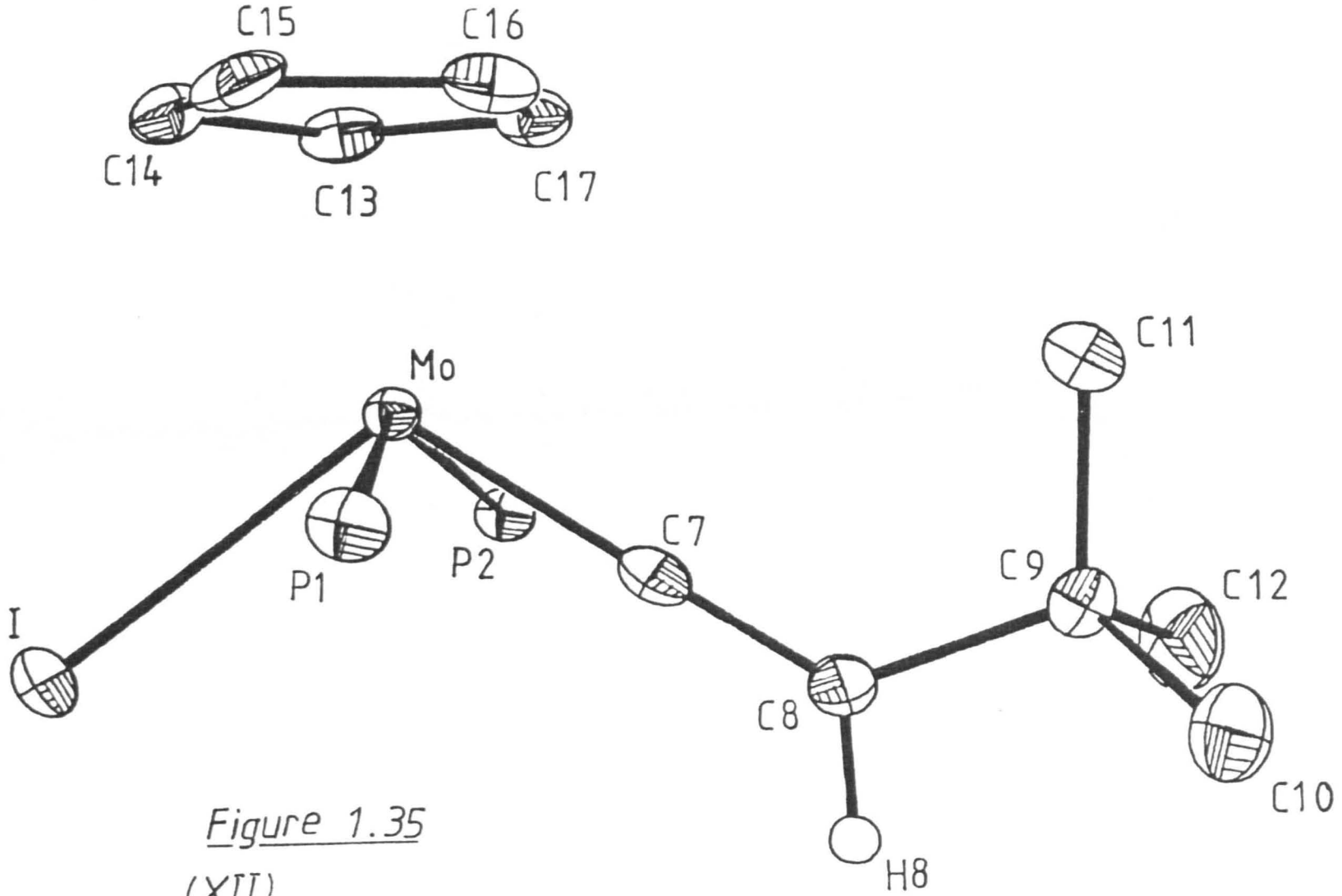


Figure 1.35

(XII)

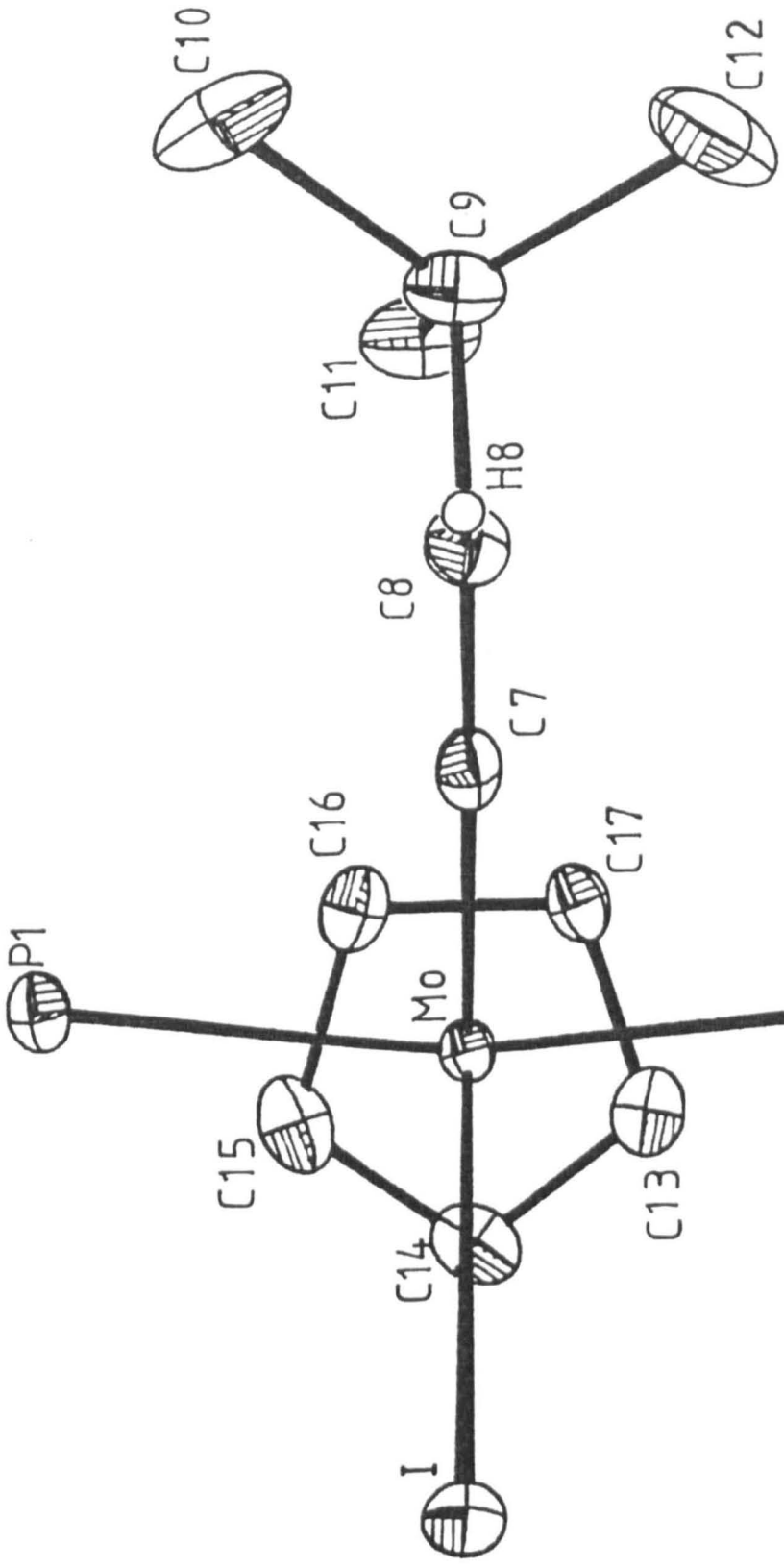


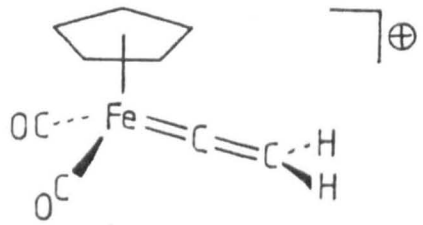
Figure 1.36

(XII)

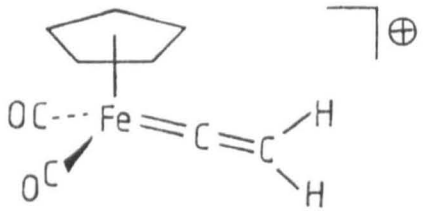
Table 1.8 Molybdenum-Iodine Bond Lengths

Compound	Mo-I, Å	Ref.
$[Mo(C{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I]$ (XII)	2.821(1)	This work
$[Mo{=}C(CH_2Bu^t)PO(OMe)_2\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$	2.823(1)	162
$[Mo(NO)(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)I]$	2.821(1)	56b
$[Mo(CO)_2(\eta\text{-}C_5H_4Me)I_3]$	2.881, 2.842, 2.859(1)	56e
$[Mo(CO)_2(\eta\text{-}C_5H_5)(COCH_2CH_2CH_2)I]$	2.862(1)	56i
$[Mo(\eta\text{-}C_5H_4\{CH_2CH_2I\})_2I_2]$	2.849(1)	163

A final point of interest for the vinylidene ligand is its orientation. The plane of the vinylidene i.e. that through [Mo-C(7)-C(8)-C(9)] is approximately normal to that of the cyclopentadienyl ring. This contrasts with the prediction from EHMO calculations by Hoffmann et al which suggest that the orientational preference of the vinylidene in the 'model' complex $[Fe(CO)_2(C{=}CH_2)(\eta\text{-}C_5H_5)]^+$ is that in which the substituents on the β-carbon atom of the vinylidene are bisected by a molecular mirror plane (A), rather than coincident with it (B).



(A)



(B)

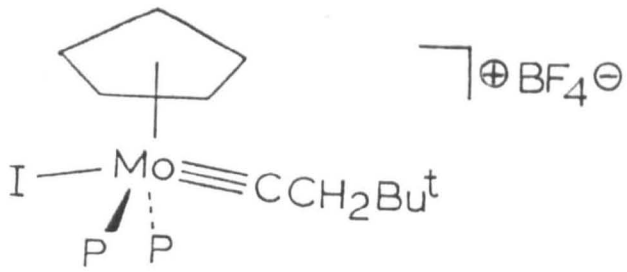
This preference is rather marginal the barrier to vinylidene rotation computed to be 3.6 kcal mol^{-1}.[165]

A crystal structure determination on $[Mn(CO)_2(C{=}CMe_2)(\eta\text{-}C_5H_5)]$[147,164] shows the vinylidene to be oriented as in (A). In $[Fe\{C{=}C(Me)CS_2Me\}(dppe)(\eta\text{-}C_5H_5)][I]$ the plane of the vinylidene forms a dihedral angle of 130.3° with the plane bisecting the $[Fe(dppe)(\eta\text{-}C_5H_5)]$ fragment.[150] Although the tilting of the vinylidene in this iron complex may be attributable to relief of steric contacts, this does not appear to be the case for $[Mn(CO)_2(C{=}CHPh)(\eta\text{-}C_5H_5)]$[133] which possesses a similar skew orientation for the vinylidene plane in the solid state. Selegue[150] concludes that there may be an electronic explanation for the vinylidene orientations found in these two compounds.

In (XII), the vinylidene is oriented as in (B), with the ^{t}butyl group 'syn' to the cyclopentadienyl ligand. This would minimise contact between the ^{t}butyl and the $[P(OMe)_3]$ ligands.

Reaction of the Vinylidene Complex $[Mo(C{=}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I]$ with $[HBF_4]$

Dropwise addition of tetrafluoroboric acid diethyletherate $[HBF_4.Et_2O]$ to a stirred red ether solution of the vinylidene complex (XII) at -78°c proceeded by rapid decolouration and the formation of a pale yellow precipitate. This was recrystallised from CH_2Cl_2:hexane to yield a microcrystalline solid (XIII). The n.m.r. data indicated the formulation of (XIII) as the cationic carbyne species $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I][BF_4]$. Preliminary x-ray studies on (XIII) confirmed this. The structure allowed the location of all non-hydrogen atoms although poor quality of the data did not allow refinement much below R = 0.20, so that a description of the structure will not be given here.



(XIII)

Protonation of (XII) thus occurs at the vinylidene β-carbon atom and parallels the protonation of the anionic vinylidene $[Mo(C{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][Li]$ to give (VI). These are the first examples of carbyne complex synthesis from vinylidene species.

The reaction between (VI) and $[CF_3I]$ (or $[C_3F_7I]$) in hexane at -30°c was found to give a third product in addition to the vinylidene (XII) and the carbene (89). Pale yellow-brown crystals were deposited on the sides of the reaction vessel as large needles, which were found not to be (VI), as suspected, due to their insolubility in hexane and ether. N.m.r. spectroscopy (CD_2Cl_2) indicated the presence of the cation $[Mo(CCH_2But)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I]$ found in (XIII).

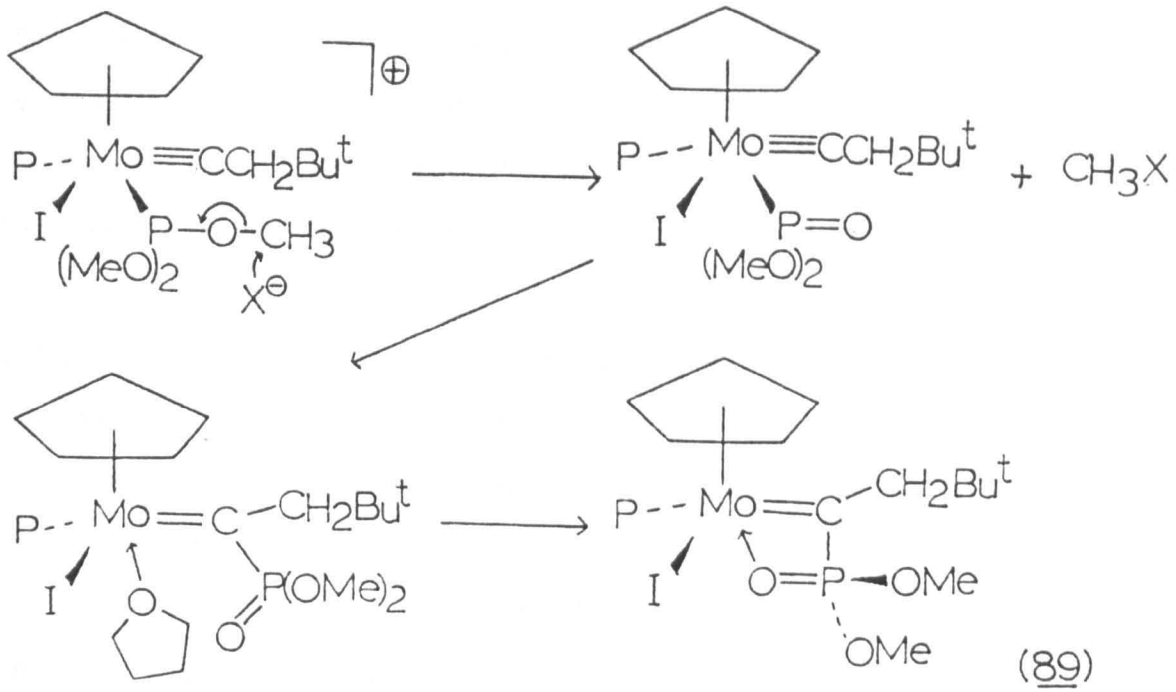
Recrystallisation from thf, which had led to the formation of crystals of reasonable size for the $[BF_4]$ salt of (XIII), was attempted. This gave an unexpected result, the solution turning deep-green over a period of several minutes. The colour change was found to be due to formation of the carbene (89). This dramatic change of reactivity compared with the $[BF_4]$ analogue must be caused by the counter-ion of the material, believed to be either $[CF_3]^-$ or $[F]^-$.

The lack of resonances attributable to either of these in the ^{13}C and ^{19}F n.m.r. spectra leave this assignment in some doubt unfortunately.

The mechanism of formation of (89) is, however, somewhat clearer (see Scheme 1.17). Reaction of $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ with $[CF_3I]$ may give the cation (XIII) by net $[I]^+$ addition. This quite possibly, in contrast to $[H]^+$ addition, proceeds by frontier rather than charge control. Nucleophilic attack of the counter-ion would then lead to abstraction of a methyl group from a phosphite ligand. (this reaction step is analogous to the Michaelis-Arbusov reaction of alkylhalides with trialkyl- phosphites), i.e.

$$P(OR)_3 + R'I \text{ -------> } [R'P(OR)_3]^+[I]^- \text{ -------> } R'P(OR)_2O + RI$$

Alkylidyne insertion into the Mo-P σ-bond of the resulting phosphonate ligand $\{P(OMe)_2O\}$ would then lead to formation of a 16 electron species possessing the carbene ligand found in the product. Coordination of the P=O oxygen would then give (89). The acceleration of the reaction in thf may derive from stabilisation of the proposed 16 electron intermediate by coordination of solvent. No appreciable conversion to (89) occurring in methylene chloride solution over a period of 1 day. It is also interesting that no vinylidene formation is observed in the thf reaction. Deprotonation of the β-carbon is thus not competing with methyl abstraction under those conditions.



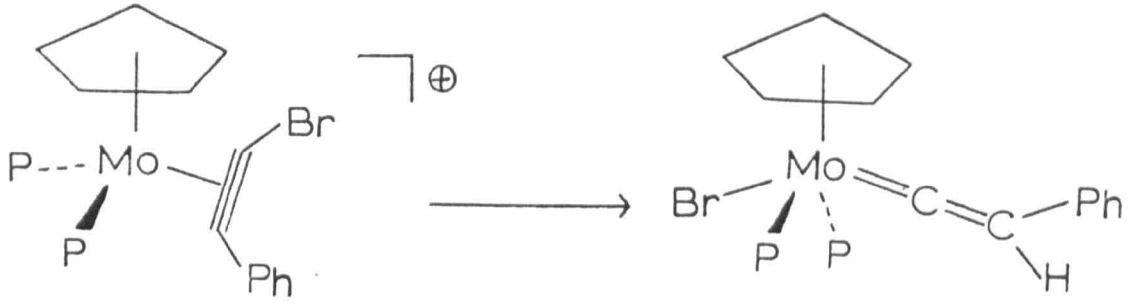
(89)

Scheme 1.17

Formation of the Vinylidene Complex [Mo(C=CHPh){P(OMe)$_3$}$_2$(n-C$_5$H$_5$)Br]

An interesting route to an analogue of the vinylidene complex (XII) was discovered in these laboratories by R.G. Beevor.[29,165]

Treatment of the 1-bromo-2-phenylethyne complex [Mo(BrC≡CPh)-{P(OMe)$_3$}$_2$(n-C$_5$H$_5$)][BF$_4$] with [KBH(Bu^s)$_3$] was found to yield a deep red-brown neutral complex, (XIV).



(XIV)

This was structurally characterised by the author and found to be the vinylidene $[Mo(C{=}CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)Br]$, shown in Figures 1.37 and 1.38. Similarities are found with the structure of (XII) which differs only in the halide bound to the metal and one of the substituents at the vinylidene β-carbon. Neither change influences the orientation of the vinylidene ligand plane, which in both cases bisects the molecule. In (XIV), the dihedral angle between the plane of the cyclopentadienyl ring and the plane of the vinylidene atoms [C(7)-C(8)-C(9)] is 90.4°.

The Mo-C(7) bond length is 1.917(5)Å, identical within error limits to the corresponding bond in (XII). The C(7)=C(8) bond length is 1.327(7)Å.

The plane of the phenyl ring is roughly coincident with that of the vinylidene, the dihedral angle between the planes [C(7)-C(8)-C(9)] and [C(9)-C(14)] is 10.1°. This conformation is presumably more stable due to conjugation of the π-systems of the vinylidene and its phenyl substituent.

The phosphite ligands are symmetrically bound to the metal, although there is no crystallographic mirror plane through the molecule. The Mo-P bond lengths are essentially equal: Mo-P(1) = 2.462(2)Å, Mo-P(2) = 2.463(2)Å. The cisoid interligand angles also show the pseudo-symmetry: Br-Mo-P(1) = 82.0(1)°, Br-Mo-P(2) = 79.7(1)°, C(7)-Mo-P(1) = 79.1(2)° and C(7)-Mo-P(2) = 79.2(2)°. The transoid angles are 142.7(1)° between the phosphites and 113.9(2)° for Br-Mo-C(7). Differences between these angles and the corresponding ones for (XII) are attributable to the smaller atomic radius (and therefore a smaller 'bite' at the metal) of bromine compared to iodine.

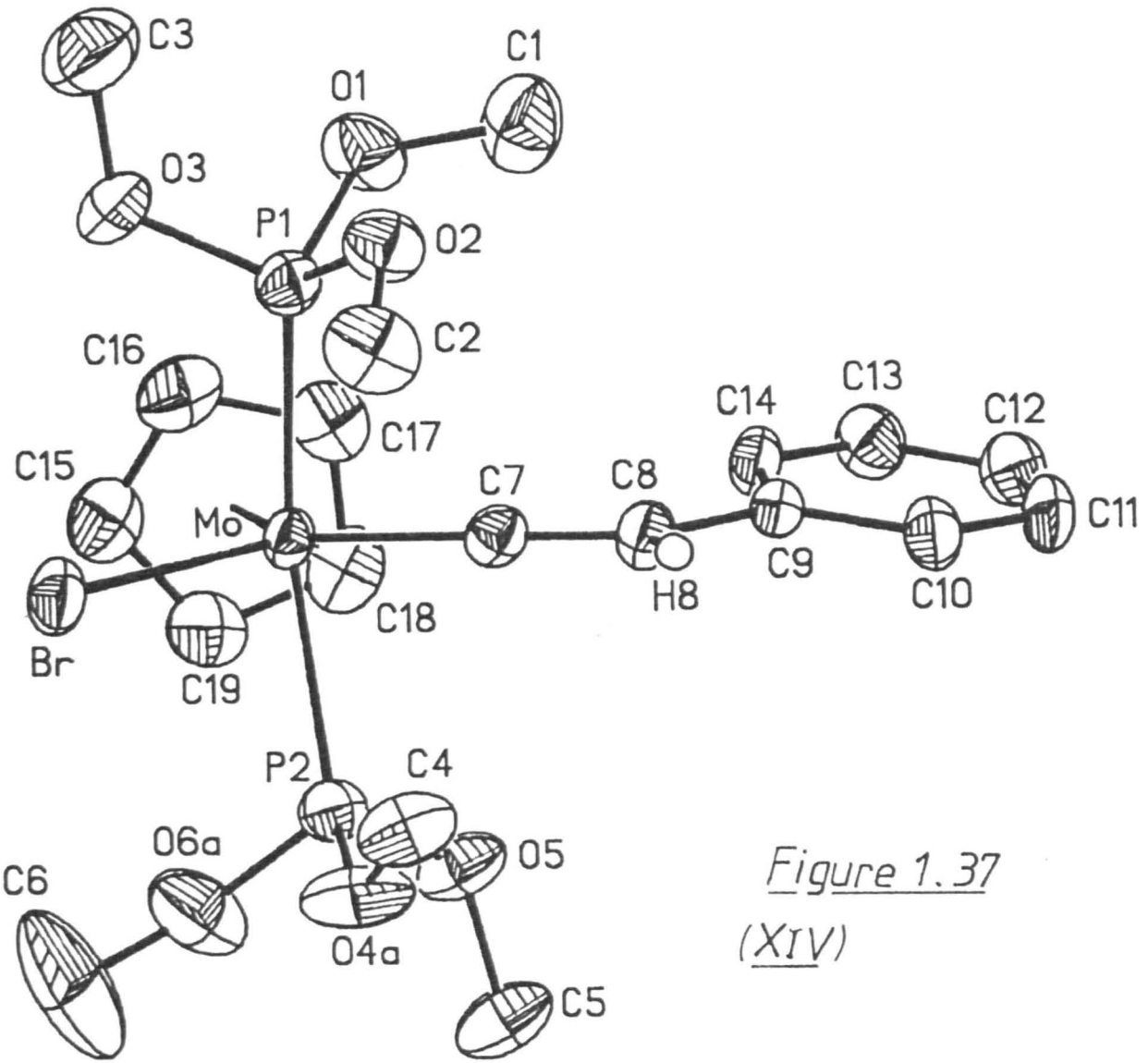


Figure 1.37

(XIV)

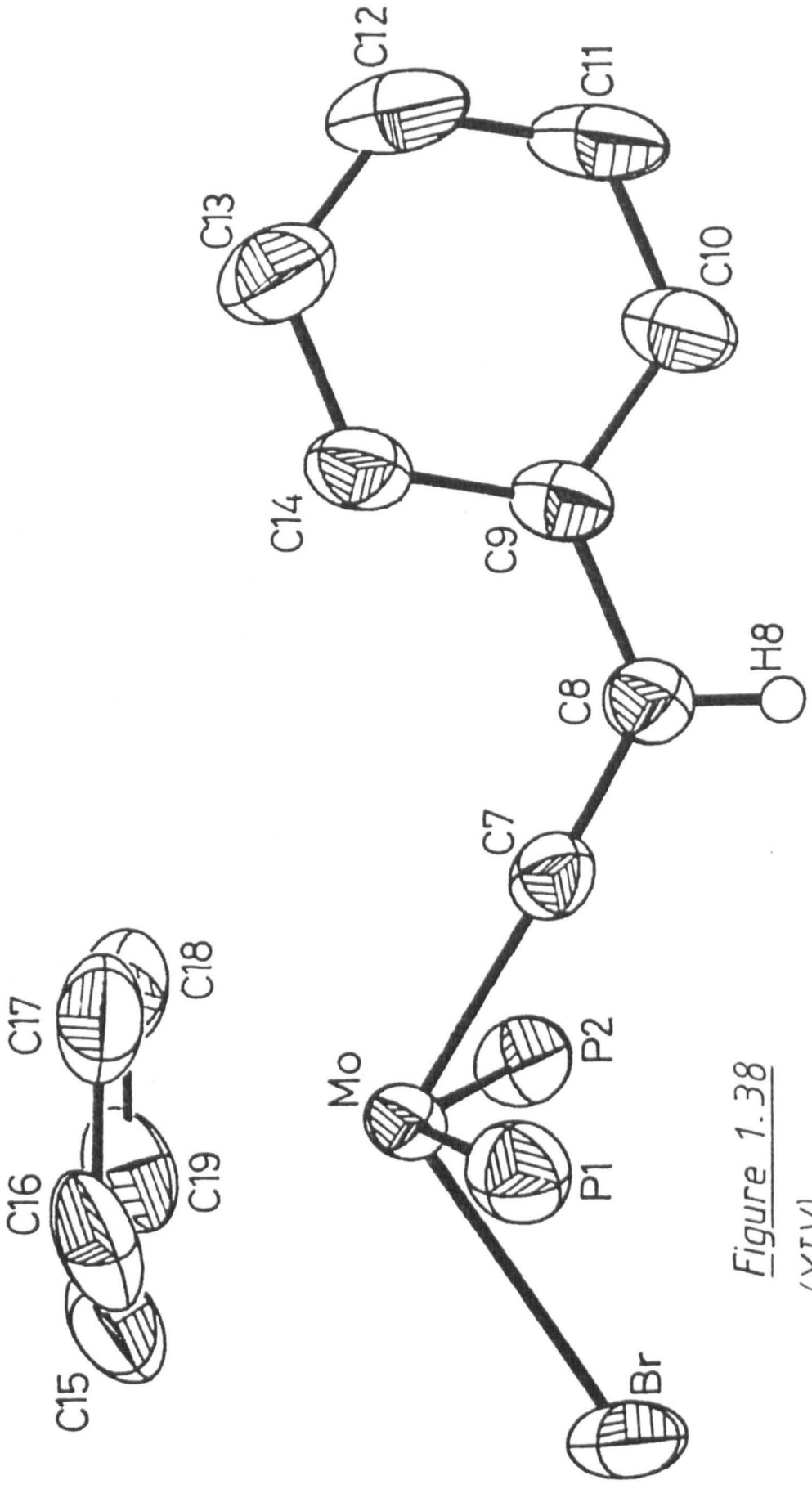


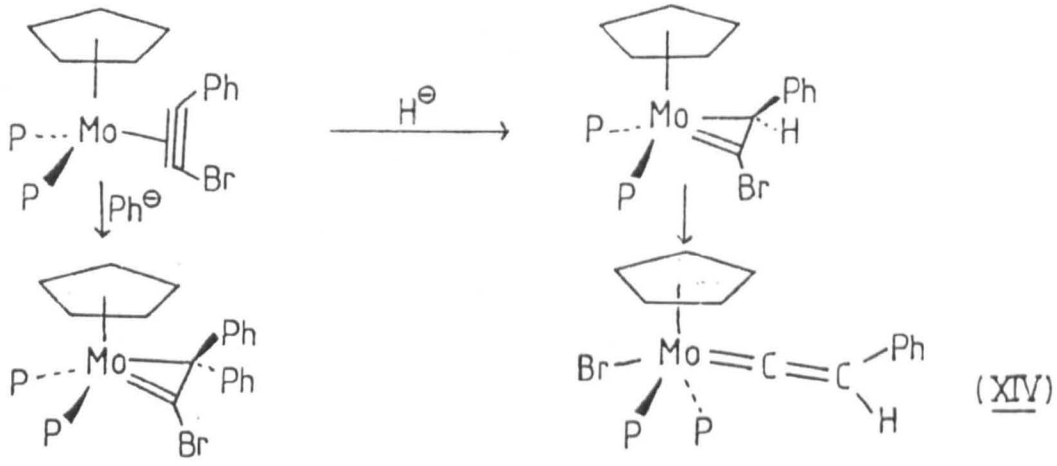
Figure 1.38

(XIV)

The Mo-Br bond length is 2.651(1)Å, nearly 0.2Å shorter than the Mo-I bond in (XII) and in accord with other Mo-Br bonds, eg that found in cis-$[Mo(CO)_2(PPh_3)(\eta\text{-}C_5H_5)Br]$ of 2.671(5)Å.[166]

Mechanism for the Formation of (XIV)

Reactions of the complexes $[Mo(RC{\equiv}CR')\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with hydride have afforded π-allyl, alkylidyne and η^2-vinyl complexes depending on the substituents R and R'. The avilability of β-hydrogens, for example when R = Me, can lead to π-allyl formation; terminal acetylene complexes, i.e. R = H, may ultimately yield alkylidynes. Absence of either α- or β-hydrogens on the alkyne usually results in the formation of stable η^2-vinyl complexes. In the case of the bromoalkyne complex initial attack of hydride probably gives a η^2-vinyl intermediate which then undergoes formal α-elimination of the bromide to give (XIV). Evidence for the involvement of a η^2-vinyl species comes from the isolation of $[\overline{Mo{=}CBr{-}C}Ph_2\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ from the analogous reaction with $[LiCuPh_2]$, i.e. a source of $[Ph]^-$.[165] (Scheme 1.17)



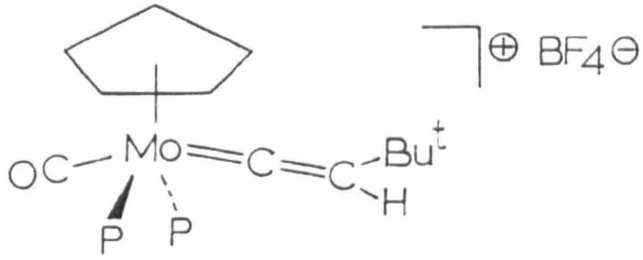
(XIV)

Scheme 1.17

Protonation of the Acetylide Complex (IV) $[Mo(CO)(C{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

Another route to vinylidene complexes, discussed in the introduction to Section 1.4, is the protonation of neutral acetylide complexes. Convenient synthesis of the acetylide complex (IV) from the reaction of $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with hydride in the presence of [CO] provided us with access to a cationic vinylidene species (XV), $[Mo(CO)(C{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.

Dropwise addition at -78°c of $[HBF_4.Et_2O]$ to an ether solution of (IV) resulted in the discolouration of the solution and formation of a pale yellow precipitate.[167] The identification of this as (XV) was based on its n.m.r. parameters. The ^{13}C spectrum displayed resonances consistent with the structure below.

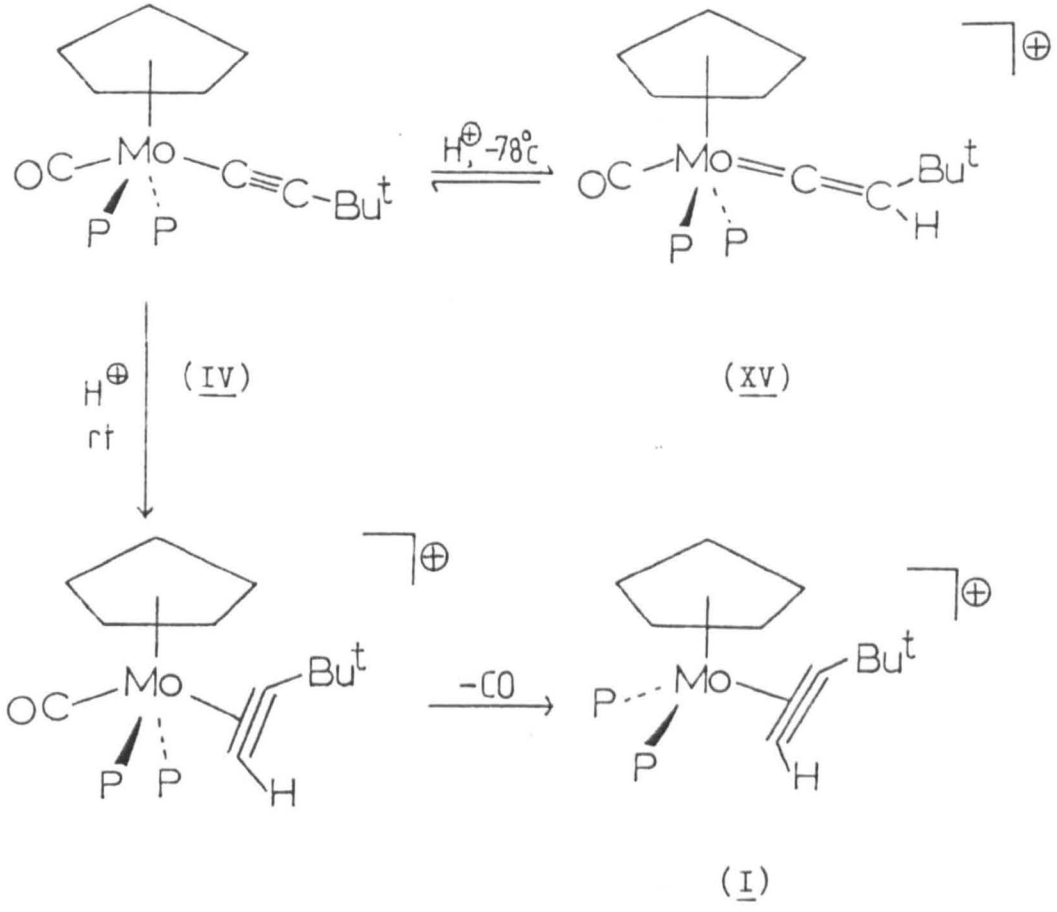


(XV)

The protonation was found to be reversible, treatment of (XV) with $[NEt_3]$ resulting in reformation of the acetylide complex (IV).

Compound (XV), was found to be thermally unstable, both in solution and in the solid state, decomposing rapidly at room temperature in solution to a purple complex, whose solubility properties indicated that it too, was cationic. This was found, unexpectedly, to be the acetylene complex $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (I).

The conversion of (XV) to (I) was interesting in view of the number of vinylidene complexes which have been formed from terminal alkyne complexes. The reaction may be understood upon finding that (XV) did not decompose to (I) at room temperature in the presence of excess acid. This suggested that (XV) was in equilibrium with its conjugate base, (IV) and that the latter was an intermediate in the formation of (I). Transformation of (IV) to (I) would occur if protonation took place at the α-carbon of the vinylidene and the cationic alkyne complex formed then lost [CO], the acetylene converting to a four electron donor ligand. (Scheme 1.18).



(I)

Scheme 1.18

The formation of the ditungsten species (83), (page 107) upon protonation of $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ may now be understood. Initial attack of $[H]^+$ may yield a vinylidene as a kinetic product. This is in equilibrium with the starting material and will allow eventual protonation at the α-carbon of the acetylide. The species $[W(CO)_3(HC{\equiv}CPh)(\eta\text{-}C_5H_5)]^+$ not only readily loses [CO] but allows substitution of a further carbonyl by the tungsten acetylide which acts as a 'pseudo-acetylene'. This reaction is not so surprising in view of the fact that synthesis of $[Mo(CO)(RC{\equiv}CR')_2(\eta\text{-}C_5H_5)]^+$ is carried out by addition of $[Ag]^+$ and two equivalents of alkyne (per Mo) to $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$. No doubt this reaction passes through the intermediate $[Mo(CO)_2(RC{\equiv}CR')(\eta\text{-}C_5H_5)]^+$, analogous to (I) but with two π-acceptor carbonyl ligands rather than two donor phosphite groups. The carbonyls destabilise these cationic complexes and so are labile to substitution by donor ligands, leading to the synthesis of compounds like (I).[20]

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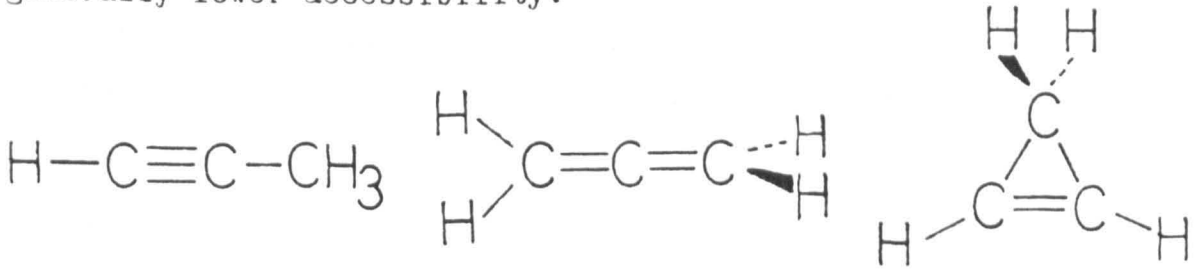
Section 2.1

Introduction

The Transition Metal Chemistry of Cyclopropenes

Both propynes and allenes exhibit a rich and extensive transition metal chemistry. Their valence ring isomers, cyclopropenes, have been less thoroughly explored in this context, perhaps due to their generally lower accessibility.



Propyne Allene Cyclopropene

Figure 2.1. Isomeric Forms of the unsaturated Hydrocarbon C_3H_4.

However, the interaction of small ring hydrocarbons, such as cyclopropanes and cyclopropenes with metal centres is of considerable interest, particularly with respect to carbon-carbon bond cleavage and formation. These being key processes in the transition metal catalysed rearrangements of small ring organic molecules.[1]

Consideration of the bonding in these molecules and their potential as ligands is of benefit in understanding how such processes may be facilitated at metal sites.

Walsh has described a model for bonding in cyclopropanes based on sp^2 hybridisation at each carbon atom.[2] The C-C bonds are formed from the intra-annular overlap of the three sp^2 orbitals which are directed to the centre of the ring, and the three in-plane p-π orbitals.

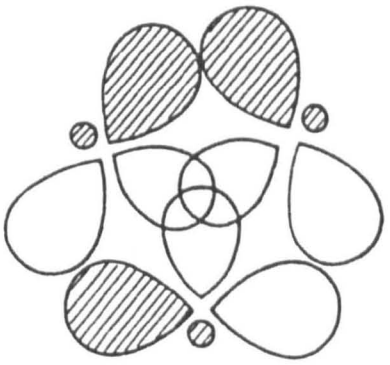
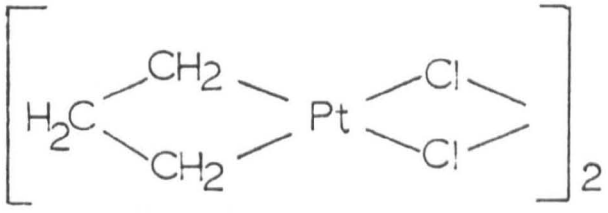


Figure 2.2. Walsh description of the Bonding in Cyclopropanes.

The remaining six sp^2 hybrids are used to form the C-H bonds.

More accurate bonding descriptions have been obtained from molecular orbital and valence bond calculations[3-5] and an attempt at unifying the the results from these different approaches has been presented.[6] Extended Huckel calculations[3] indicate that the HOMO's in cyclopropane are a degenerate pair composed almost entirely of carbon 2p (p_x and p_y) orbitals in the ring plane. The other orbital associated with ring bonding is low lying and has a large contribution from the carbon 2s orbitals.

One of the earliest reports of the reaction of a cyclopropane with a transition metal species came from Tipper[7] who prepared a 1:1 adduct of dichloroplatinum and cyclopropane,(1). The product was later shown to be a platinacyclobutane complex.[8]



(1)

The insertion of the platinum moiety into the carbon-carbon bond of the cyclopropane ring presumably results from a synergic interaction involving -donation from one of the HOMO's of the cyclopropane to a vacant metal hybrid orbital of σ-symmetry and π-retrodative bonding from the metal to the cyclopropane LUMO (which is the antibonding combination of the in-plane (p_x,p_y) carbon p orbitals).

Figure 2.3. Interaction of a C-C Bond of Cyclopropane with a Metal Centre.

The effect of this is to cleave the carbon-carbon bond and form two metal-carbon σ-bonds. This is directly analogous to the Dewar-Chatt-Duncanson model for metal-olefin bonding (see page 1).

With respect to symmetry arguments, the scheme in Fig. 2.3 could in principle be applied to account for the cleavage of any C-C σ-bond. That this is only observed in reality for cyclopropanes and other 'strained' molecules is a direct result of the relatively high energy of the HOMO σ-donor and low energy of the LUMO σ*- acceptor orbitals in these species compared with unstrained hydrocarbons.

The above bonding analysis for cyclopropanes may readily be adapted and extended to cyclopropenes. Two of the ring carbons now only bear one substituent and may be considered sp hybridised.

Since these substituents lie in the plane of the ring the C-H bonding has no contribution from the p_z orbitals. These out-of-plane orbitals thus overlap to form a π- bond between the carbons (C_1 and C_2).

Cyclopropenes, therefore, have two orthogonal pairs of orbitals which may be used in metal-ligand bonding. A similarity exists in this respect between cyclopropenes and acetylenes (c.f. the frontier orbitals of cyclopropene, Fig. 2.4 and those for acetylene, page 2).

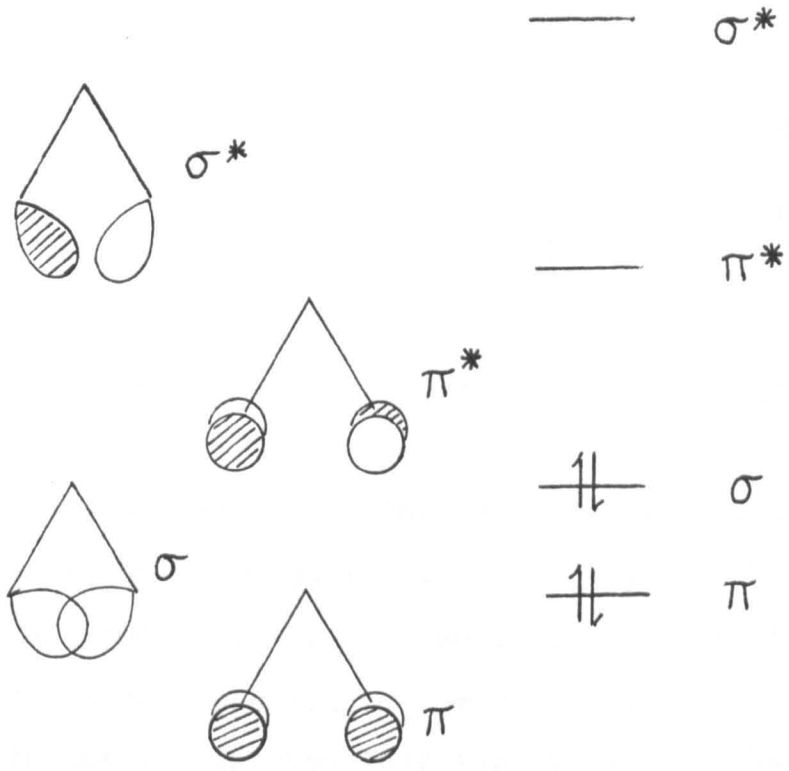


Figure 2.4. Principal orbitals of Cyclopropenes available for bonding to Transition Metals

In acetylenes, however, the orthogonal pairs are degenerate, which is not so for cyclopropenes. The ordering of the levels in Fig. 2.4 is based on Hoffmann's calculations for the cyclopropenyl cation in a ground state geometry.[9]

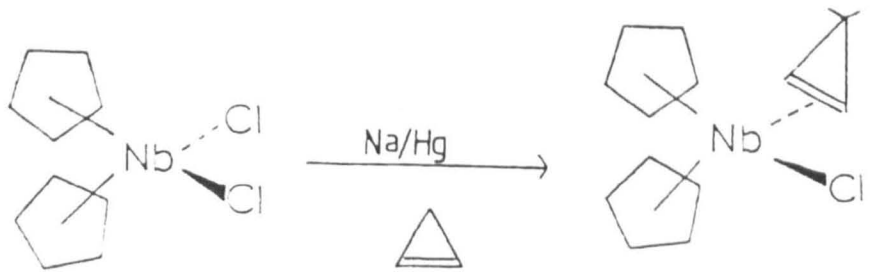
How, then, do cyclopropenes interact with metal centres ? Although somewhat rare, there are several examples in which cyclopropenes are π-bound to metal centres as though they were ordinary olefins.

The platinum(0)ethylene complex (2) reacts with cyclopropenes to yield the products (3),[10] certain examples of which have been structurally characterised.[11]

(2) P = PPh_3 (3)

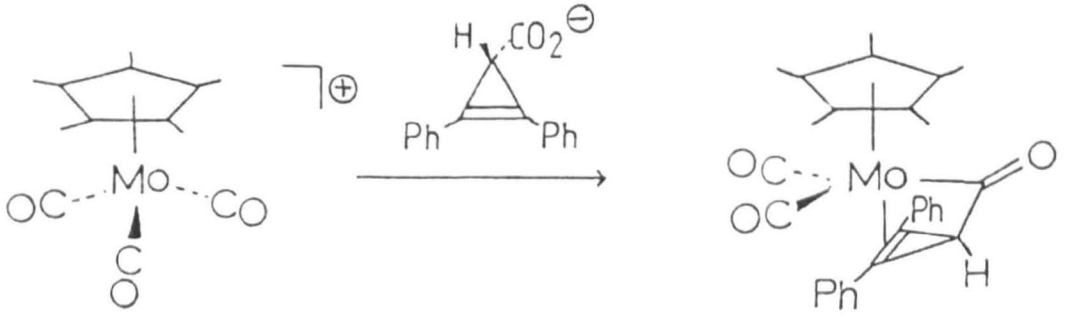
The geometrical changes of the cyclopropene ligand upon complexation are quite substantial. The C_1-C_2 bond has been lengthened to 1.50Å from 1.30Å in the parent molecule,[12] indicating a formal reduction of the C-C bond order from two to one. This may also be compared with the C-C internuclear separation of 2.54Å in the platinacyclobutane complex $[Pt(C_3H_6)(py)_2Cl_2]$, the bis(pyridine) adduct of (1).[8] In (3), the atoms C_1 and C_2 are coplanar with the platinum and phosphorus atoms, such that the metal has an effective trigonal geometry. The substituents on C_1 and C_2 are not exactly normal to this plane, but are bent away from the metal. These facts are consistent the idea of the cyclopropene acting as a η^2-coordinated olefin.

Reaction of $[NbCl_2(n\text{-}C_5H_5)_2]$ with cyclopropene following sodium amalgam reduction yielded (4).[13] Upon treatment with hydrochloric acid, (4) gave cyclopropane in nearly quantitative yield; this selective hydrogenation suggesting that ring cleavage had not occurred at any point.



(4)

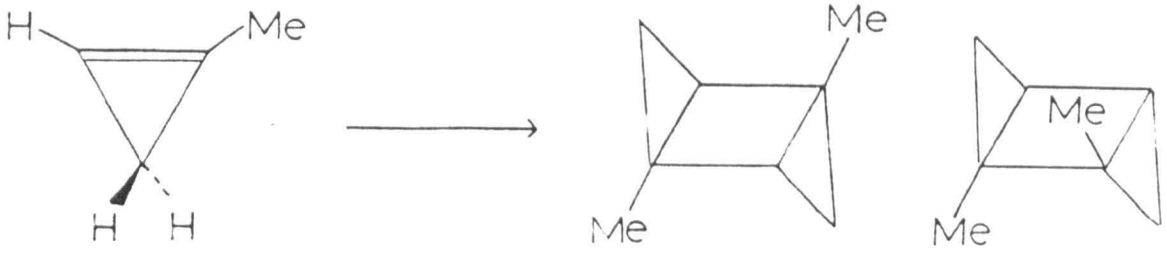
Recently Hughes et al. have characterised an n-cyclopropene complex of molybdenum from the following reaction.[14]



Coordination of cyclopropene in the above manner is often postulated as the first step in many other reactions of cyclopropenes with transition metal species, which do not result in simple adduct formation; for example in cyclopropene oligomerisations.

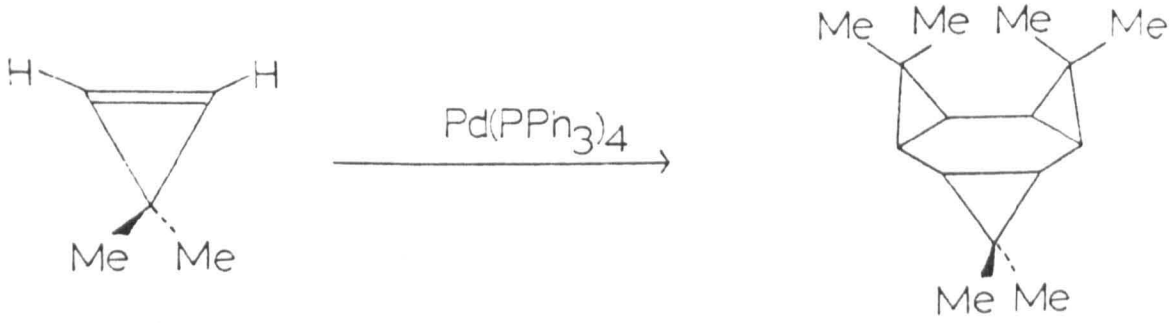
These reactions fall into two categories; one involving retention of the ring (cyclo-oligomerisation), the other, ring opening (linear oligomerisation).

The earliest example of a reaction in the first category was the cyclo-dimerisation of 1-methylcyclopropene by palladium (II) catalysts.[15]



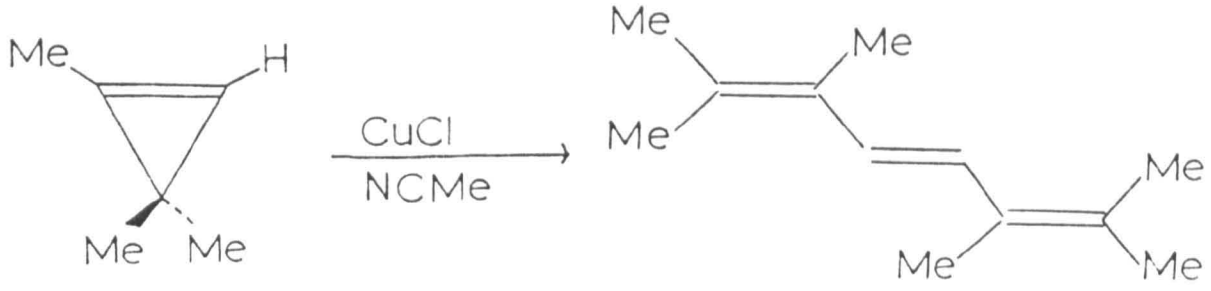
(5a) (5b)

Following this, Binger et al. reported the nearly quantitative cyclo-trimerisation of 3,3-dimethylcyclopropene to (6) by $[Pd(PPh_3)_4]$,[16] and less selective cyclo-oligomerisations (though catalytic) by various other Pd (0) complexes, in which the products ranged from cyclo-dimers to tetramers.[17]

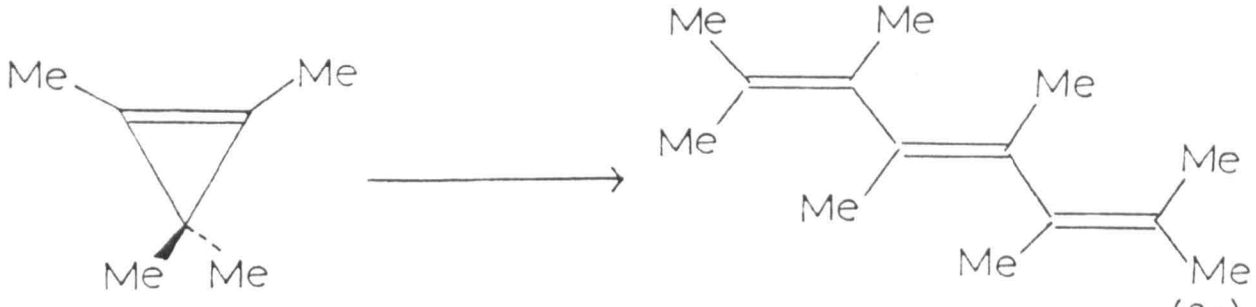


(6)

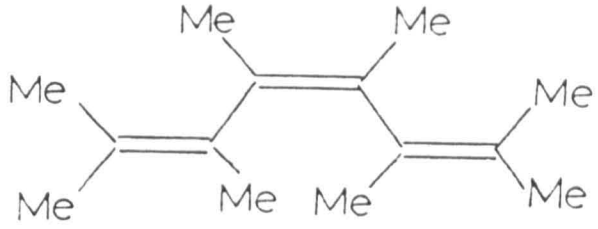
Pre-dating all this was the observation by Stechl[18] of the 'linear' dimerisation of tri- and tetramethylcyclopropenes by a copper (I) chloride catalyst, in which the octatriene complexes (7) and (8) are formed respectively.



(7)

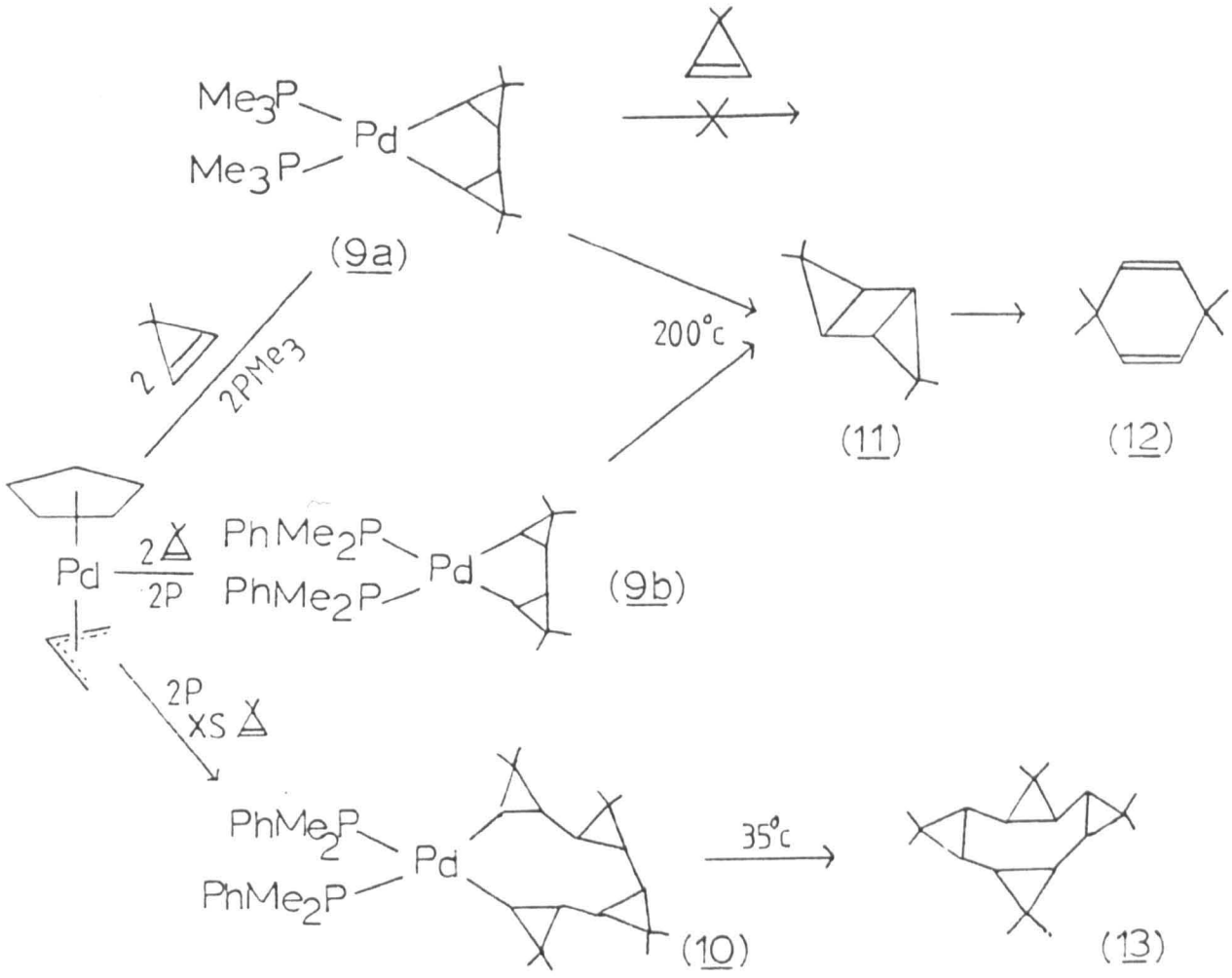


(8a)



(8b)

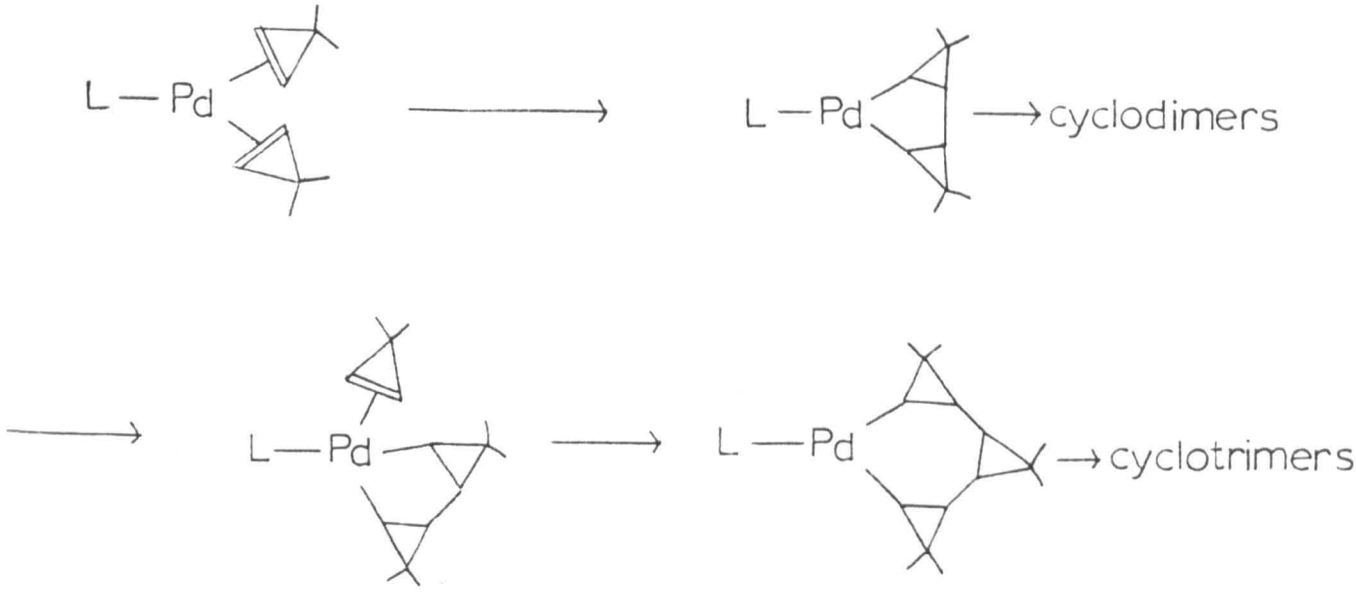
Clearly two different mechanisms are in operation in these oligomerisations. Key intermediates in the cyclo-oligomerisation process appear to have been isolated recently by Binger and co-workers.[19] By reaction of $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ with 3,3-dimethylcyclopropene in the presence of phosphines, they have succeeded in preparing the palladacycloalkanes (9) and (10). Although these are stable at room temperature, the cyclotetramer (13) is readily eliminated from (10) in refluxing diethyl ether.



The palladacyclopentanes (9) need more vigorous conditions for cleavage to occur, under which the presumed elimination product, the tricyclohexane (11), isomerises to the observed cyclohexadiene (12).

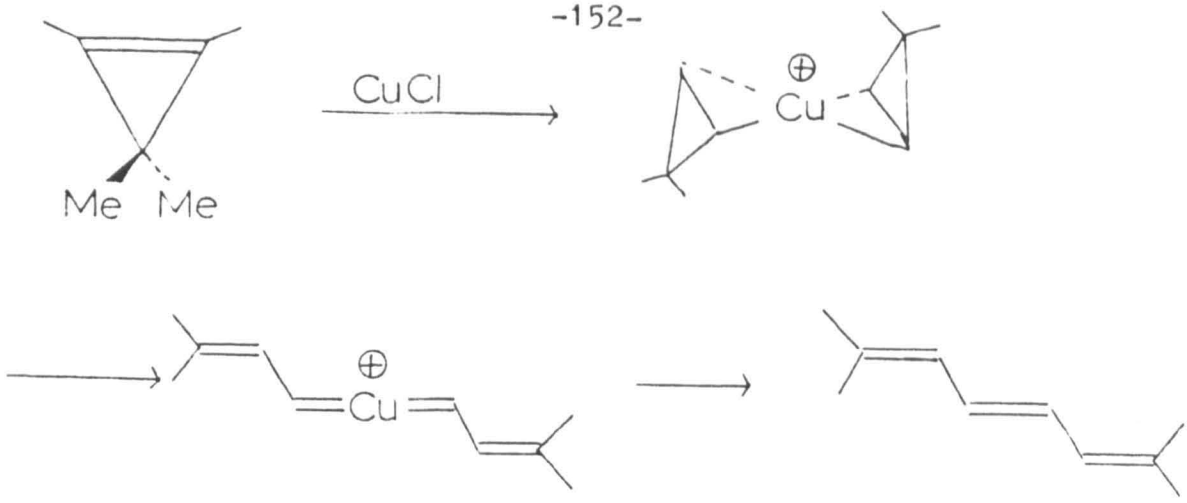
Compounds such as (9) are probably formed from precursors comprising two cyclopropene ligands bound to the metal in the manner proposed for (3). A reductive elimination step may then be envisaged, in which two Pd-C bonds are broken and a new C-C bond linking the two C_3 rings, is formed.

Whether a second reductive elimination to yield the cyclo-dimer, or further addition of cyclopropene to produce the higher oligomers then takes place, is presumably a function of the particular system.

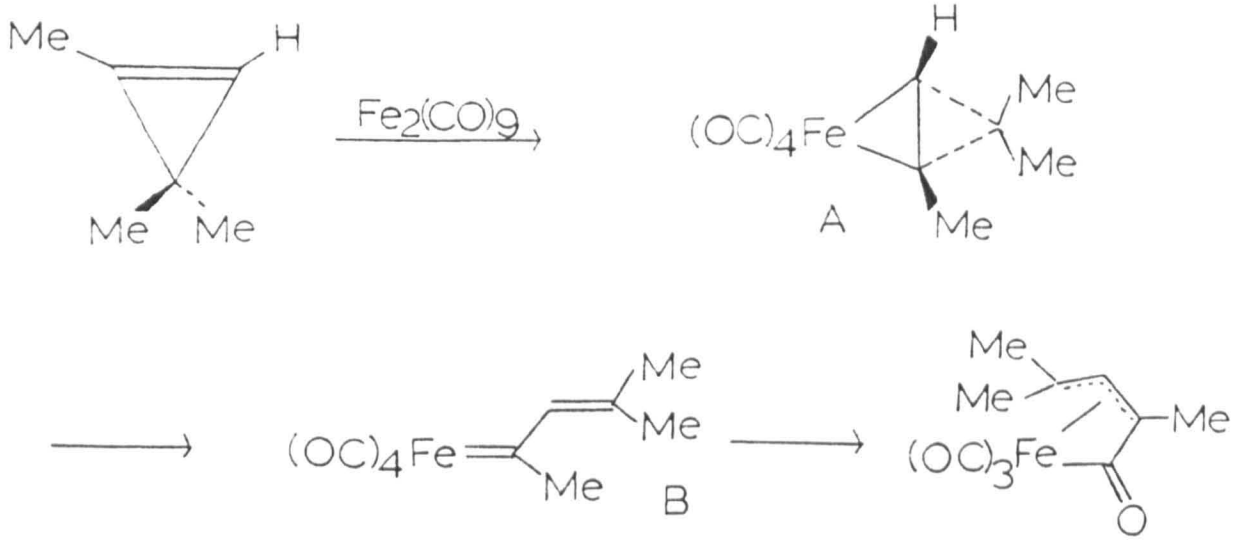


Although the above scheme may account in principle for the formation of all the cyclo-oligomers, other mechanisms may be at work. Thus the anticipated ring expansion of (9b) to (10) on treatment with two equivalents of cyclopropene was not observed.[19] Formation of (10) and hence cyclotetramerisation appear therefore to be occurring *via* an alternate pathway, for example one in which more than one metal centre is involved.

The process observed by Stechl must be different, as ring opening must be accounted for. His original mechanistic postulation involved the intermediacy of a copper bis(η^1-vinylcarbene) species, which by linking of the carbene moieties and reductive elimination provides an explanation of triene formation. No evidence was obtained as to whether the reaction was intra- or inter-molecular in nature, however.

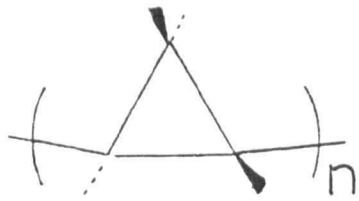


Evidence for η^1-vinylcarbene formation by metal-assisted cyclopropene ring opening comes from several sources, though no stable mononuclear metal complexes containing this functionality have been isolated by this route. Such a species is strongly implicated as an intermediate in the synthesis of (14) from $Fe_2(CO)_9$ and 1,3,3-trimethylcyclopropene.[20]

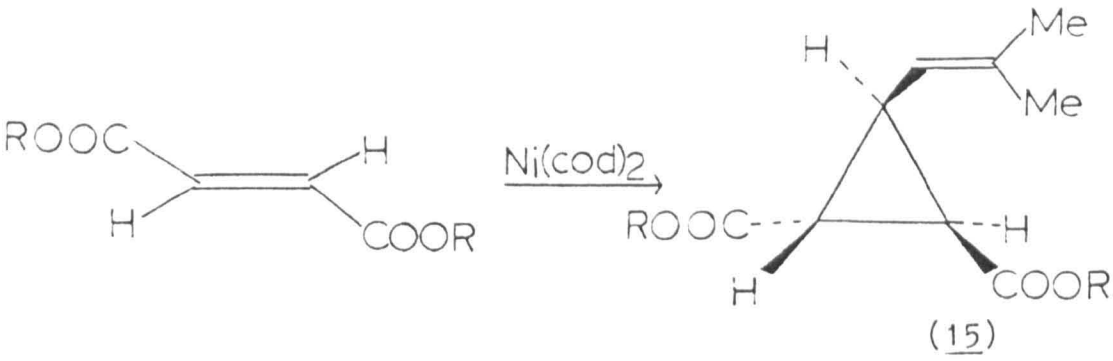


It is likely that the above reaction proceeds via A and B; i.e. initial coordination of the cyclopropene to a 16-electron $Fe(CO)_4$ unit, followed by ring opening, carbonyl 'insertion' into the iron-carbene bond and π- complexation of the allylic moiety thus formed.

Binger and McMeeking have also provided some evidence for the nature of these ring opening reactions. Although $[Ni(cod)_2]$ was observed by them to polymerise cyclopropenes affording chains of the type shown below, carrying out the reaction in the presence of certain



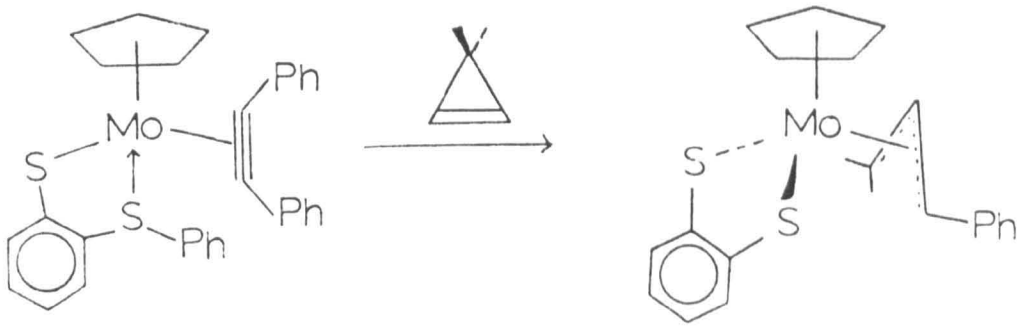
substituted olefins yielded the cyclopropene-olefin adducts (15).[21]



(15)

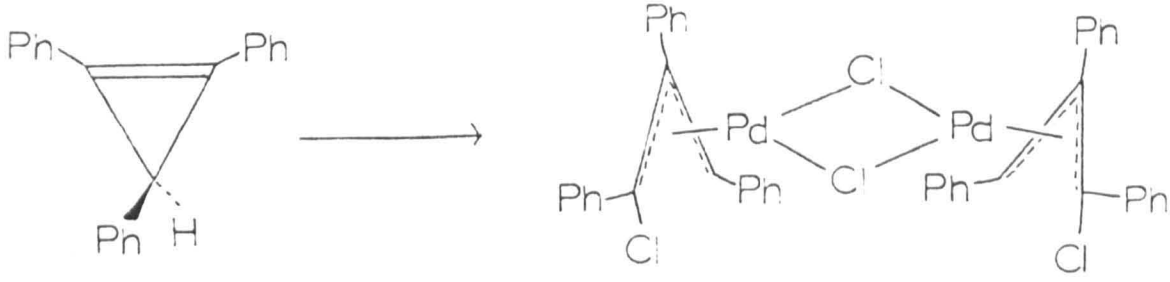
These compounds appear to be the result of carbene addition across the olefinic double bond, a well-known reaction in cyclopropane synthesis.[22]

Other cyclopropene ring opening reactions have been observed at metal-centres which have been accompanied by interesting molecular rearrangements. For example $[Mo(C_2Ph_2)\{SC_6H_4o\text{-}S(C_6H_5)\}(\eta\text{-}C_5H_5)]$(16) reacts with 3,3-dimethylcyclopropene to yield the π-allyl complex (17).[23]



(17)

Chloro-substituted π-allyl complexes are produced from the reaction of $[Pd(NCMe)_2Cl_2]$ with cyclopropenes.[24] It is thought that this involves carbene insertion into a Pd-Cl bond.



The mechanism by which ring opening occurs in these reactions is unknown, though a parallel may be drawn to the thermal isomerisation of bicyclobutanes to butadienes, which proceeds in a stereospecific manner.[25] Woodward and Hoffmann have indicated that this stereochemistry observed by Closs is that expected for the only symmetry allowed concerted process, in which one ring opens in a conrotatory manner and the other in a disrotatory sense.[26]

In conclusion cyclopropenes react at metal-centres in a variety of

ways, their high degree of unsaturation being the source of their potential for forming transition metal complexes.

The Chemistry of μ-Alkylidene Transition Metal Complexes

The chemistry of the class of organometallic compounds possessing a bridging methylene (CR_2) function have been the focus of much recent research. The many reasons for this have been expounded by one of the pioneers of the field in a comprehensive review article.[27]

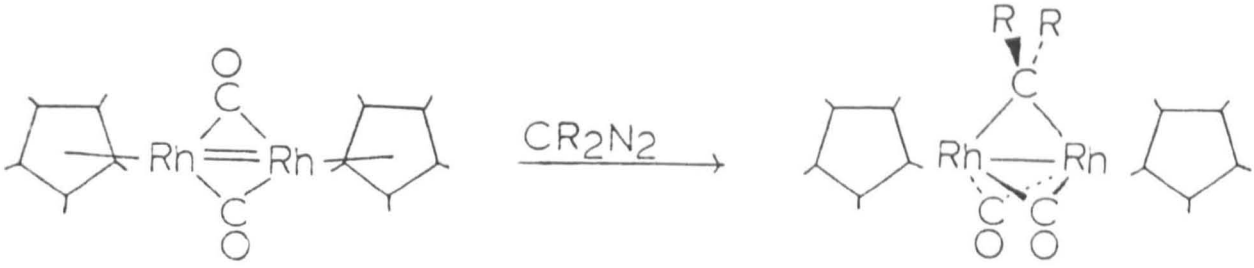
Present evidence suggests that bridging alkylidene complexes are more stable than their carbonyl analogues (when these counterparts are known)[28]. As a vast range of (μ-CO) complexes do exist, the implication that future activity in this area may exceed that of the present appears well-founded.

The Synthesis of μ-Alkylidene Complexes

Future expansion in this particular chemical arena may only be realised, however, if sufficient development and extension of existing synthetic routes to μ-alkylidene complexes (and innovation of new ones) occurs.

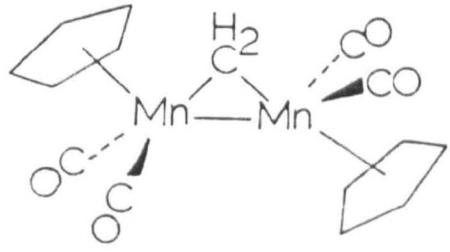
Presently these compounds may be accessed by several established approaches, the most direct of which involves the reaction of carbene precursors, such as diazoalkanes (CR_2N_2) with either unsaturated metal-metal bonded species, or metal complexes possessing labile donor ligands which may be substituted by the carbene.

Hence treatment of the rhodium dimer $[Rh(\mu\text{-}CO)(\eta\text{-}C_5Me_5)]_2$ (18), with diazoalkanes yields the compounds (19).[29] Under the right conditions these may isomerise to the singly bridged μ-carbenes, or lose one equivalent of CO to reform the Rh-Rh 'double-bond', giving structural analogues of the starting material in which one of the bridging carbonyls has been replaced by a bridging carbene ligand.



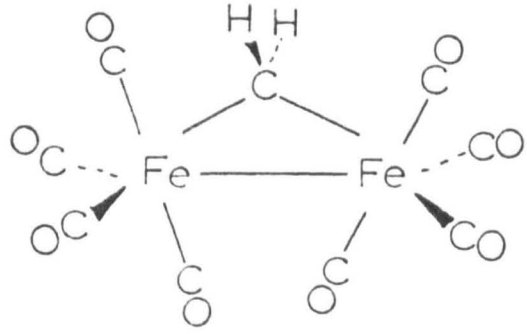
(18) (19)

The first synthesis of a complex with the 'parent' (CH_2) methylene bridge was accomplished by addition of diazomethane at low temperature to the solvento- complex $[Mn(CO)_2(THF)(\eta\text{-}C_5H_5)]$, from which the compound (20), rather than the expected mono-nuclear carbene is produced.[30]



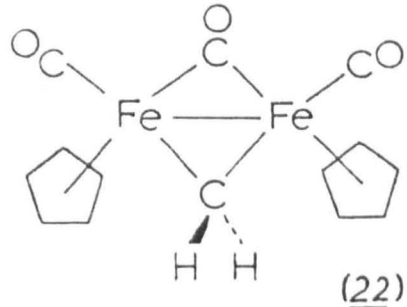
(20)

Carbene precursors other than diazoalkanes have been utilised in μ-alkylidene synthesis, though often side-reactions have reduced expected yields drastically. Geminal dihaloalkanes have met with limited success; halogen transfer to the metal centres being the main problem. One successful example is the reaction of the carbonyl anion $[Fe_2(CO)_8]^{2-}$ (as its disodium salt) with di-iodomethane to yield (21), $[Fe_2(CO)_8(\mu\text{-}CH_2)]$ in 60%.[31]



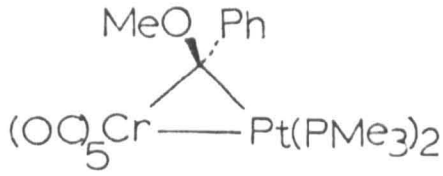
(21)

Ziegler et al have employed the Wittig reagent $Ph_3P{=}CH_2$ in the preparation of (22) from the iron dimer $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$. Compound (22) is produced in 50-60% yield as a 3:1 ratio of the geometric cis and trans isomers.[32]

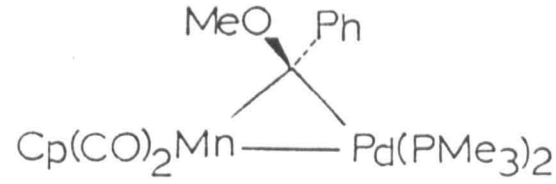


(22)

A different methodology has been used by Stone and co-workers which has allowed the synthesis of many hetero-binuclear transition-metal methylene and methylidyne complexes, a review of which has appeared.[33] This breakthrough was based on the premise that 'Fischer' type M=C and M≡C systems should react with zero-valent platinum species and other low-valent, coordinatively unsaturated complexes in a similar fashion to the C=C and C≡C functionalities of alkenes and alkynes. Two examples representative of the resulting compounds are (23) and (24).[34,35]

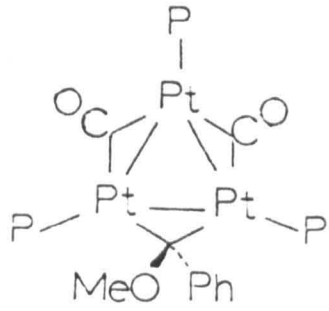


(23)



(24)

Some of these species display interesting decomposition pathways, which provide access to otherwise unattainable η-alkylidene complexes. The compound (23) fragments at temperatures greater than 80°c to give $[Cr(CO)_5(PMe)_3]$ and the homo-trinuclear platinum complexes $[Pt_3(\mu\text{-}CO)_2\{\mu\text{-}C(OMe)Ph\}(PMe_3)]$ and $[Pt\{\mu\text{-}C(OMe)Ph\}(PMe_3)]_3$, compounds (25) and (26) respectively.[36]



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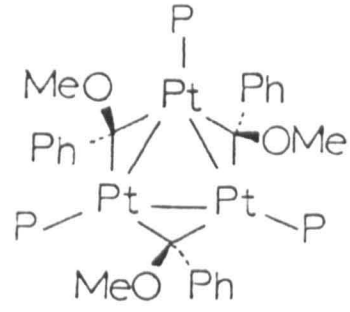
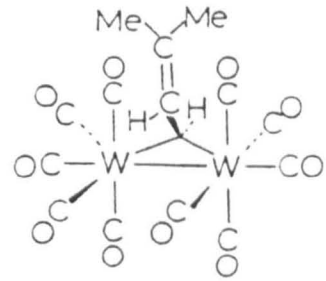


(26)

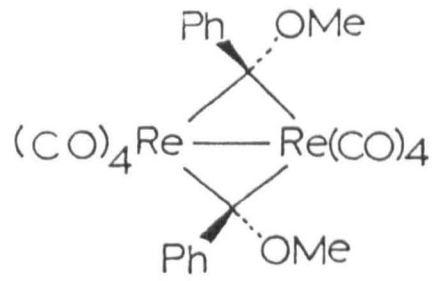
The mononuclear alkylidene complex $[Mo(CO)(NO)\{C(OMe)Ph\}(\eta\text{-}C_5H_5)]$ has been observed to transfer its carbene functionality in its reaction with $[Ni(CO)_4]$, producing $[Ni(CO)_2\{\mu\text{-}C(OMe)Ph\}]_3$, an analogue of (26).[37] It is likely that the reaction proceeds *via* the intermediate $[Mo(CO)(NO)(\eta\text{-}C_5H_5)\{\mu\text{-}C(OMe)Ph\}Ni(CO)_3]$.

Fischer-type carbenes have also been used in the preparation of homo- binuclear μ-alkylidene species; Rudler and coworkers have prepared $[W_2(CO)_{10}(\mu\text{-}CH.CH.CMe_2)]$, (27), which was incorrectly formulated as the octa-carbonyl complex due to an error in the x-ray structure determination.[38] Compound (27) is obtained in 20% yield upon treatment of $[W(CO)_5\{C(OEt)Me\}]$ with methyl-lithium followed by protonation with trifluoroacetic acid. The mechanism of its formation is unclear but is believed to involve both $[W{=}CR_2]$ and $[W{=}C{=}CR_2]$ complexes.



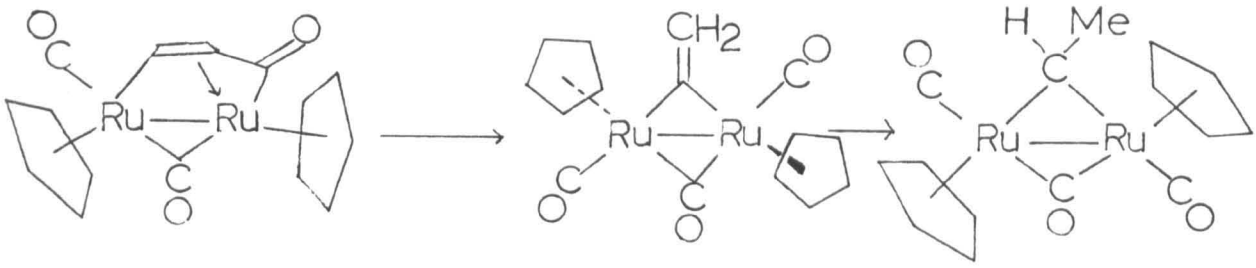
(27)

The Fischer route to mononuclear carbene synthesis,[39] seems to have potential for μ-alkylidene synthesis when the technique is applied to dimetallic or cluster carbonyl complexes. The rhenium bis(μ-alkylidene), (28) is formed when either $[Re_2(CO)_9\{C(OMe)Ph\}]$ or rhenium decacarbonyl is treated with excess phenyl-lithium and subsequently methylated.[40] Presumably the final product results from an isomerisation of the dimer $[Re(CO)_4\{C(OMe)Ph\}]_2$ which possesses two terminal alkylidene moieties.



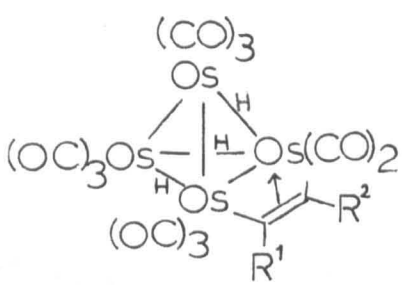
(28)

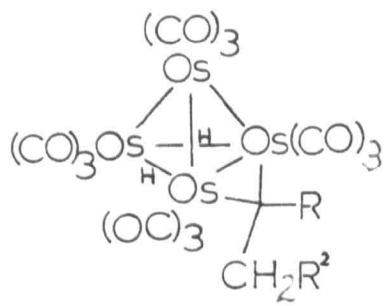
Knox et al. have observed μ-carbene formation from alkyne complexes. Compound (29), the photolysis product of $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$ and acetylene, isomerises to the μ-vinylidene (30) on toluene reflux. Sequential proton and hydride addition to either (29) or (30) then affords cis- and trans- isomers of (31) as the ultimate products.[41]



(29) (30) (31)

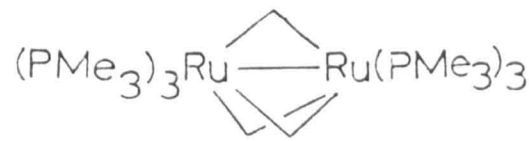
Hydrogen transfer to the β-carbon of a (μ-{η^2-vinyl}) complex has been observed by Lewis et al. during the carbonylation of (32), thus producing the μ-carbenes (33).[42]





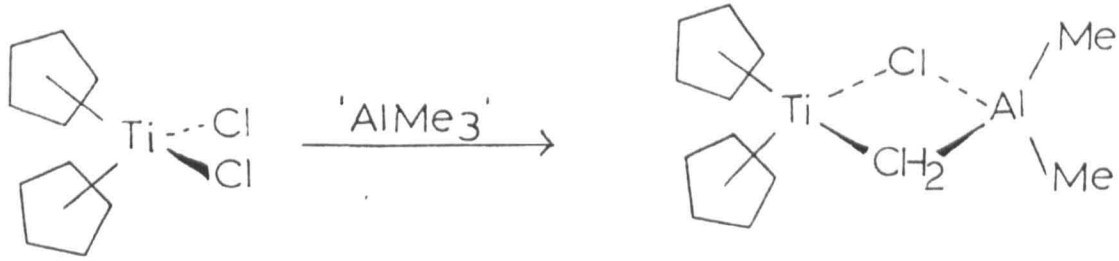
(32) (33)

An interesting but seemingly isolated example of the formation of a tris(μ-alkylidene)diruthenium complex has been communicated by the Wilkinson group.[43,44] Treatment of either $[Ru_2(O_2CMe)_4Cl]$, or better still, $[Ru_3(O_2CMe)_6(OH_2)_3(\mu_3\text{-}O)][O_2CMe]$ with excess dimethylmagnesium and PMe_3 results in the formation of (34), $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ in up to 25% yield. A mechanism involving α-hydrogen abstraction is postulated.



(34)

Tebbe has reported the first example of a methylene bridge between a main-group and a transition metal, (35), $[Ti(\eta\text{-}C_5H_5)(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$, prepared from titanocenedichloride and $[Al_2Me_6]$.[45]



(35)

Bonding in μ-Alkylidene Complexes

Before discussing their chemical reactivity, it is worthwhile to first consider the nature of the bonding in these complexes, a subject which has been treated in several recent theoretical papers.

Hoffman has carried out molecular orbital calculations on the system $[Rh_2(\mu CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$.[46] For the purposes of the study, it was beneficial to break the compound down to various fragments, the orbitals of which were well-known and then interact these to obtain the final picture. Two $[Rh(CO)(\eta\text{-}C_5H_5)]$ units were thus used to construct the unbridged trans-dimer, the frontier orbitals of which are shown on the left of Fig. 2.5. These consist of filled π_{xy} and σ- orbitals and an empty π^*_{xy}. Methylene, (CH_2), may be considered to have an sp^2 hybridised carbon with a filled hybrid orbital in the plane of the substituents, which may act as a σ-donor, and an empty p orbital, orthogonal to this plane which has π-acceptor capability.

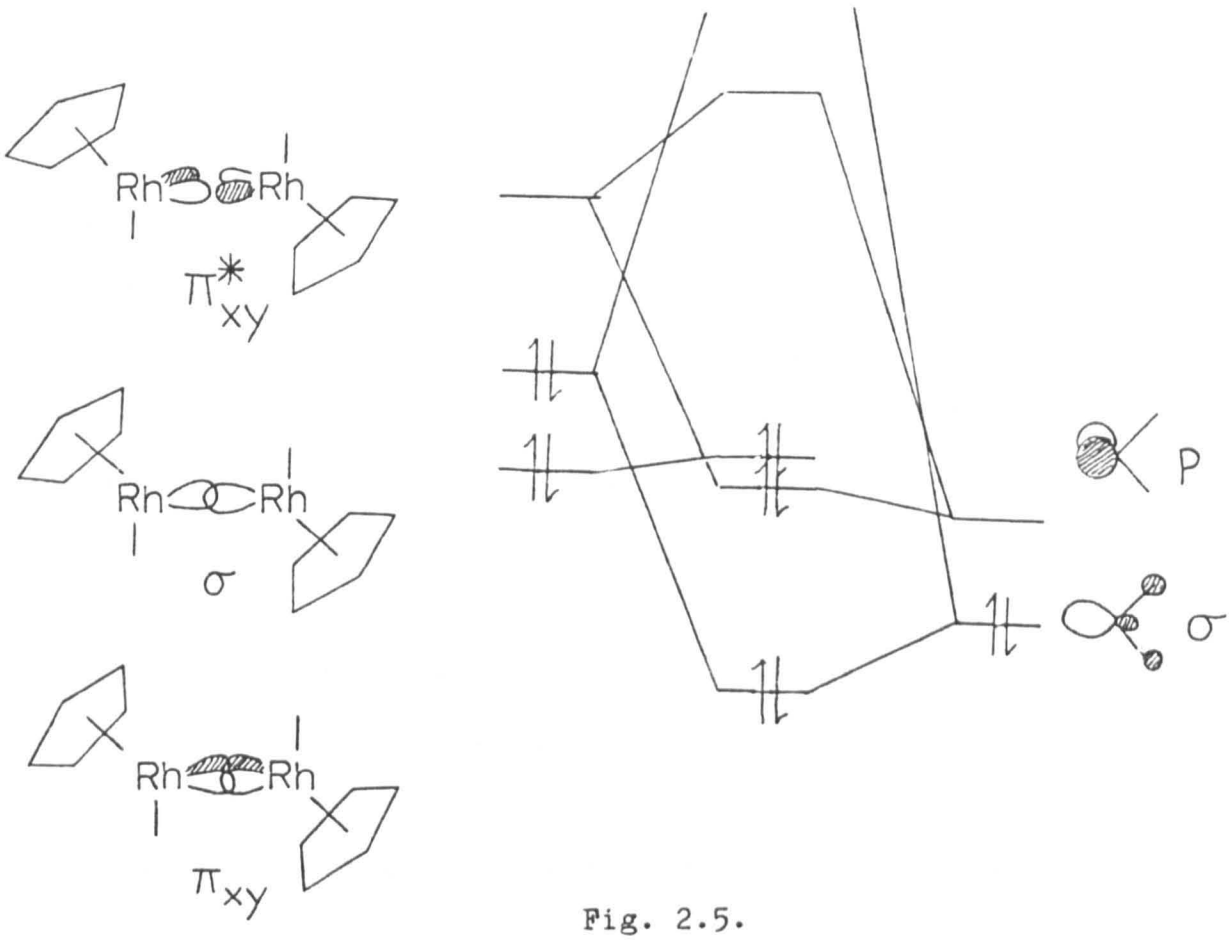


Fig. 2.5.

The bonding interactions of CH_2 with the dirhodium fragment are illustrated in Fig. 2.5; the two orbitals of σ-symmetry may add in a bonding or antibonding sense. Only the former combination of which becomes filled in the product. The two empty π^*_{xy} and p orbitals mix similarly when the methylene is oriented such that the plane of the substituents is transverse to the metal-metal vector. Again the bonding combination becomes filled and the antibonding one empty. The overall effect has been to transfer an electron from the Rh-Rh σ-bond to an orbital comprising its π^*_{xy} component. Hence the metal-metal bond order is reduced from two to one (a net bond remains as the filled π_{xy} orbital has scarcely been perturbed). Four electrons are involved in the bonding of the CH_2 group to the metal centres, such that two Rh-C single bonds have been formed and the ring system may be described as a dimetallacyclopropane.

Other theoretical investigations include one by Hoffmann et al.[47] which, for a series of $[M_2L_{10}]$ complexes, concludes that methylene groups are both better donor and acceptor bridges than carbon monoxide.

Calculations carried out by Lichtenberger et al.[48] reveal that the bridging carbene carbon in (20), $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, is associated with a region of high electron density, thus making it nucleophilic in character, in contrast to 'Fischer' type carbenes in which the polarisation ($M^{\delta-}\text{-}C^{\delta+}$) is found.[49] These findings are supported by experimentally observable evidence, Clemente et al. having performed a difference electron density determination on (20) from low temperature x-ray data which gives a maximum at the carbene carbon of $-0.78eA^{-3}$.[50]

The high degree of negative charge on this atom appears to stem from the low energy of the methylene p orbital, relative to the filled metal orbitals. Charge transfer thus takes place from the metal HOMO to the methylene p orbital when the two fragments interact.

Reactivity of μ-Alkylidene Complexes

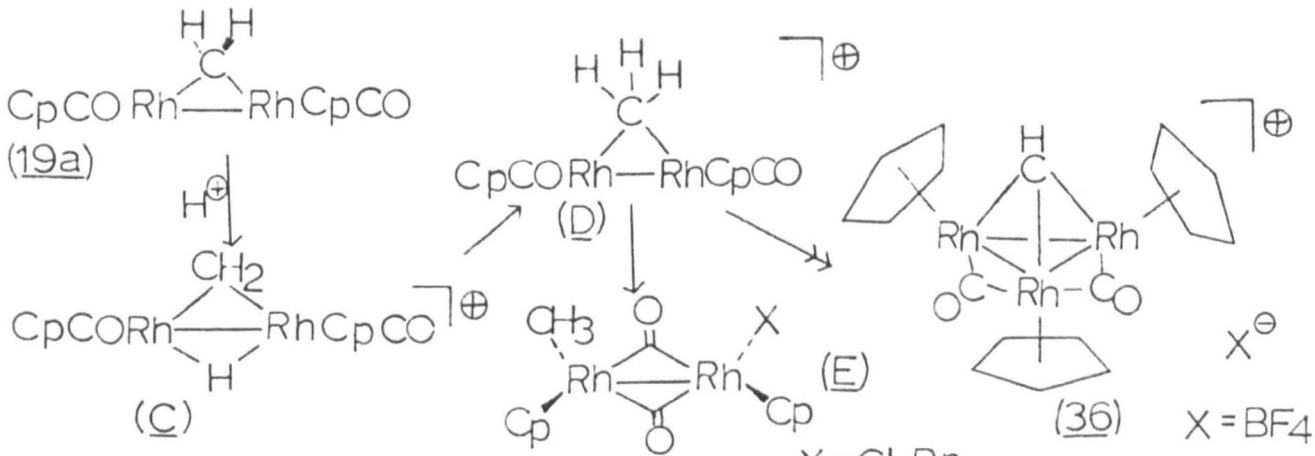
The theoretical findings and predictions about μ-carbene complexes appear to be borne out in their reactivity.

Many compounds of this class are resistant to both thermal and photolytic decomposition, though fragmentation of the dimetallacyclopropane ring is possible. Evidence for this comes from Bergman et al.[51] in the form of a 'cross-over' experiment. When a mixture of the complexes $[Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_4R)_2]$, (R=H,Me), are refluxed in benzene the mixed species $[Co(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4Me)]$ is also found to be present.

The observation by Knox et al. of cis-trans isomerisation for $[Ru_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$,[52] may involve a process in which ring bonds are broken and reformed, the authors prefering a mechanism of bridge-terminal carbene exchange, rather than one in which the carbene remains bridging and the carbonyls interchange via a semi-bridged pair.

This finding is rather surprising in that stronger ring bonding would be predicted for μ-alkylidene complexes of the second row transition-metals. The attempted synthesis of the Co-Rh species $[Co(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)Rh(C_5Me_5)]$ from the dirhodium and dicobalt analogues using Bergman's 'cross-over' principle was unsuccessful; a failure ascribed to the greater stability of the Rh-Rh system.[53]

In view of the electron rich nature of the μ-carbene moiety it would be anticipated that this class of compounds should react with various electrophiles. Although the first row transition-metal μ-alkylidene complexes (20) and (22) are resistant to even strong protic acids, the protonation reactions of several other μ-carbene species have been reported. Attack may occur at either the M-M bond or at the carbene centre. An example of the former is cited by Herrmann and coworkers.[54] Treatment of the dirhodium methylene complex (19a) with the acids HX, (X= BF_4, CF_3CO_2, CF_3SO_3, FSO_3) in THF results in the formation of the trirhodium μ_3-methylidyne complexes (36). (Scheme 2.3.)



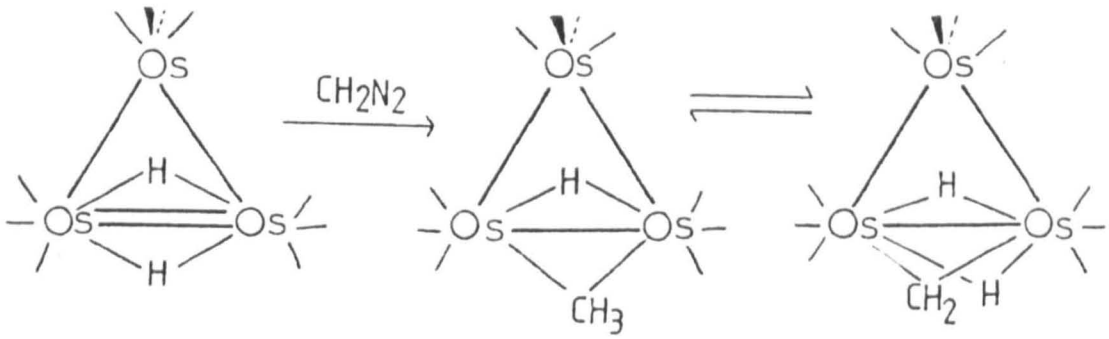
Scheme 2.3

Spectroscopic data on the intermediate (C), which may be precipitated if the reaction is carried out in diethylether, suggest it has the bridging methylene/hydride structure shown. This would indicate that the initial step is protonation of the metal-metal bond. Proton transfer (tautomerism) to yield the bridging methyl species (D), followed by several intermolecular steps involving loss of methane and hydrogen are postulated to account for the formation of the product (36).

Evidence for the possible intermediacy of the μ-methyl complex comes not only from the characterisation of the compounds (E) (which are formed when the conjugate base of the acid is a halide ion),[55] but also from the results of other protonations.

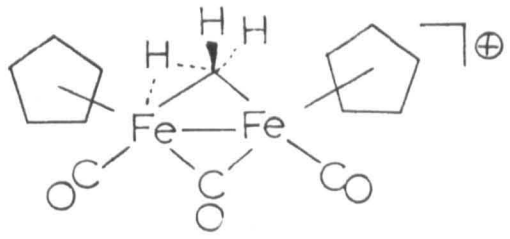
The tris-(μ-methylene)diruthenium complex (34) may be either singly or doubly protonated, yielding the $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$ and $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CH_3)_2(PMe_3)_6]^{2+}$ mono- and dications respectively.[43,44]

At first sight these complexes appear to be electron deficient. However, that the bridging methyl moiety may be able to provide more than one electron for ligand bonding, thereby alleviating the deficiency, has been elegantly demonstrated by Calvert and Shapley.[56] They have provided evidence, primarily from deuterium labelling studies, of an asymmetric mode of bridging for the methyl group in $[Os_3(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_{10}]$, (37). This species is in fluxional equilibrium with the methylene/hydride complex $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$, (38), afforded by addition of diazomethane to $[H_2Os_3(CO)_{10}]$.



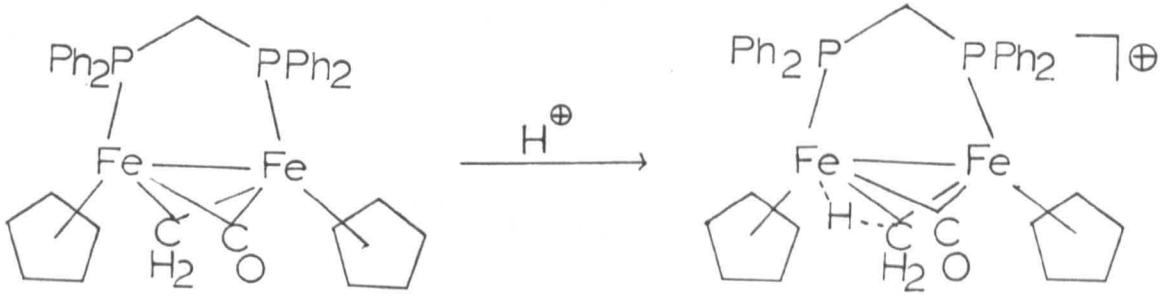
(37) (38)

Casey et al. have postulated that the protonation product, (39), of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ also possesses an asymmetric methyl bridge.[57]



(39)

Firmer evidence for this mode of bridging for a methyl group has been provided by Stone et al.[58] Addition of $[HPF_6]$ to a phosphine bridged analogue of the di-iron complex used by Casey, (40), results in the formation of (41). The structure of this compound in both solution and in the solid state has been investigated by nmr labelling experiments and low temperature x-ray and neutron diffraction studies, all of which confirm the asymmetric nature of the $(\mu\text{-}CH_3)$ ligand.



(40) (41)

Protonation of μ-methylene complexes thus provides some insight into the activation of C-H bonds by transition metals, which is currently an important goal of much organometallic research.

Interest in bridging carbene complexes has also been generated by the implication that surface carbene species are intermediates in the Fischer-Tropsch reaction, whereby a mixture of saturated and unsaturated hydrocarbons and oxy-organic compounds are produced catalytically by the passage of CO and H_2 at high pressure over various metal surfaces.

Key evidence for the involvement of carbenes comes from the work of Brady and Pettit.[59] They have shown that the product distribution resulting from a diazomethane/H_2 reaction on several metal surfaces bears a strong correlation to that observed for CO/H_2 mixtures.

The reaction of μ-alkylidene complexes with both hydrogen and unsaturated hydrocarbons such as olefins and alkynes is therefore of interest in relation to the Fischer-Tropsch process.

Pettit et al. have investigated the reactions of $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ with hydrogen and ethylene, the main organic products from which are methane and propane respectively.[60]

$$Fe_2(CO)_8(\mu\text{-}CH_2) \xrightarrow{H_2,\ 11\,atm} CH_4\ 81\%,\ CH_3CHO\ 5\% + Fe_3(CO)_{12}$$

$$\xrightarrow[20\,atm]{C_2H_4} CH_3CH{=}CH_2 + Fe(CO)_4(C_2H_4)$$

Reaction of μ-alkylidene complexes with alkynes, may however lead to the formation of μ-allylidenes, which are bridging carbenes possessing a vinyl sustituent which is additionally bound to one of the metal centres.

μ-Allylidene Complexes

As defined here, μ-allylidene complexes are those transition metal compounds containing a (μ-{η^1,η^3 vinylcarbene}) moiety, as shown in Fig. 2.6.

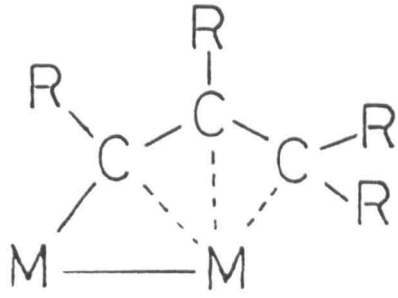
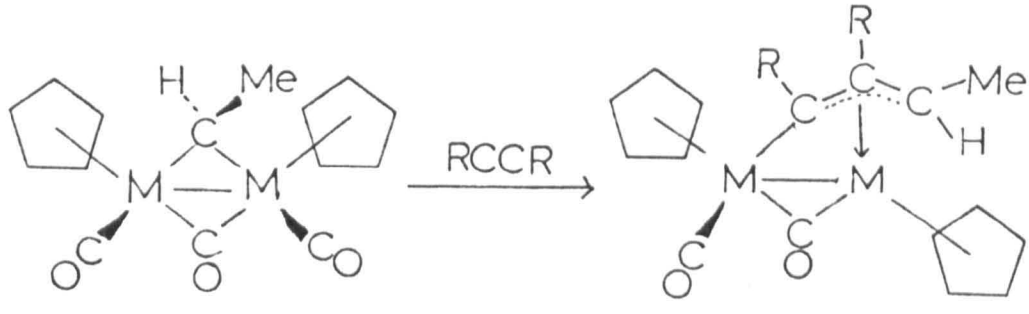


Fig 2.6.

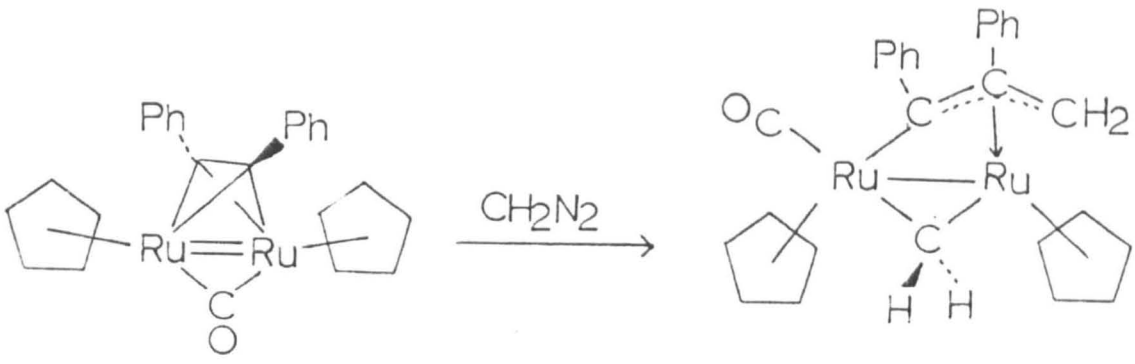
Unreported before 1980, several examples of this special class of bridging carbene complex have now appeared in the literature. They are commonly synthesised by C-C bond forming reactions between unsaturated organic ligands at dimetal centres, though ring opening of cyclopropenes offers an alternative route in which the carbon framework is preformed.

Knox et al. have reported the preparation of μ-allylidene complexes by a variety of C-C bond forming reactions. Addition of acetylenes to μ-carbene complexes is one approach, used to synthesise the iron and ruthenium compounds (42).[60]



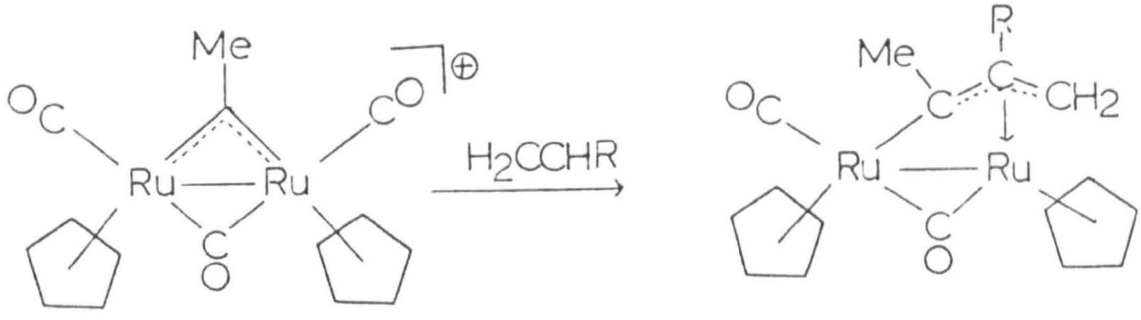
(42)

In an elegant reversal of this proceedure a similar product (43) may be prepared by the reaction of a (μ-acetylene) complex with diazomethane.[61]



(43)

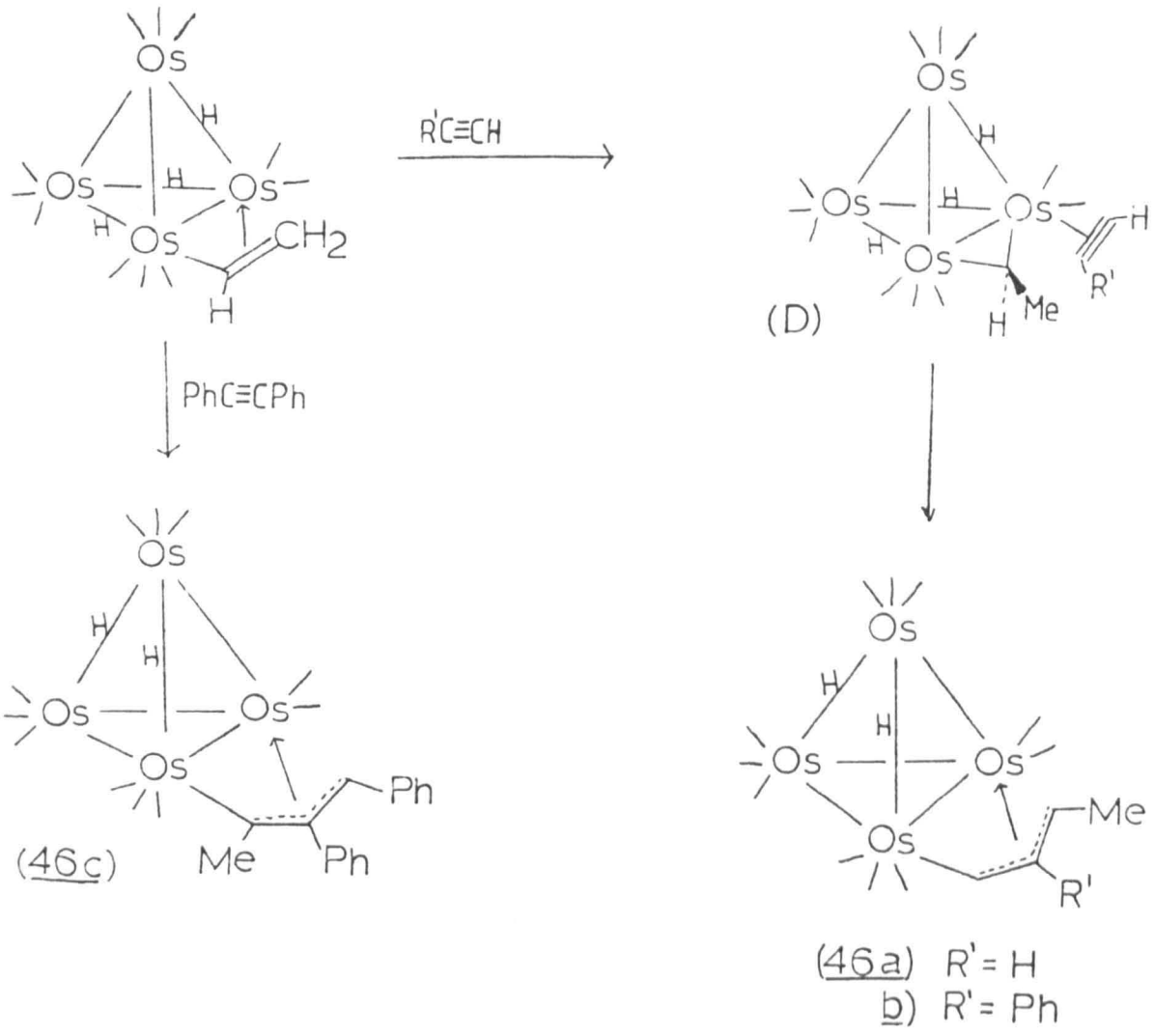
Another alternative is the addition of olefins to the cationic μ-alkylidyne complex (44) which yields the neutral allylidene complexes (45).[62]



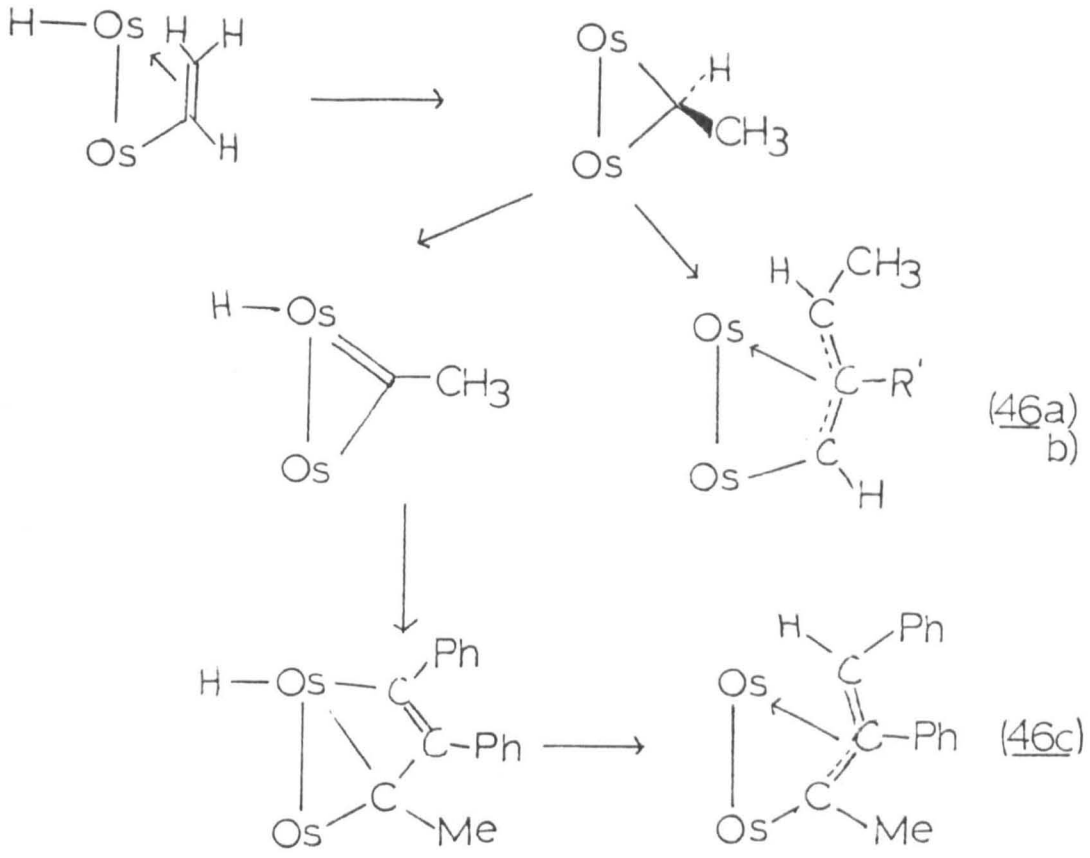
(44) (45)

Reaction of the μ-vinyl complex (32a) with acetylenes yields the stoichiometric addition products (46).[16] In the case of C_2H_2 and HCCPh the μ-allylidene products (46a) and (46b) have the regiochemistry expected from the insertion of the acetylene into the μ-carbene (D),

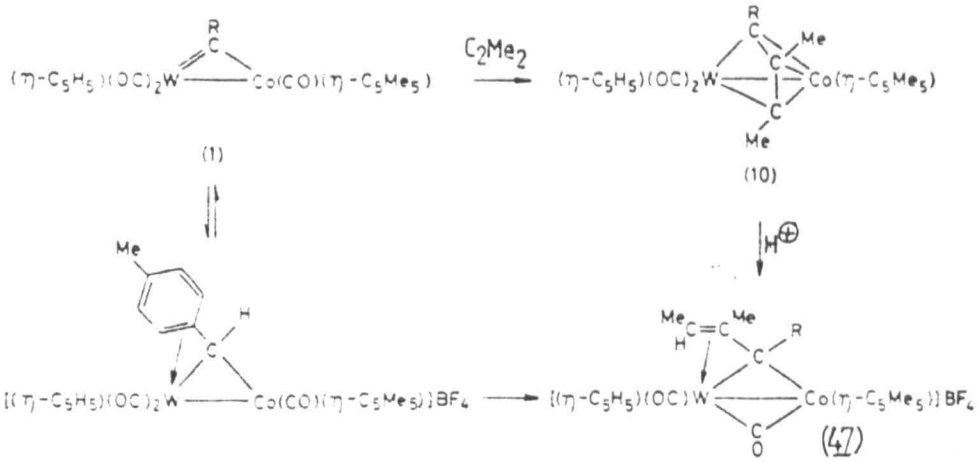
which by analogy with the carbonyl adduct (33) would be formed on coordination of the acetylene.



Diphenylacetylene produces a μ-allylidene with a different regiochemistry (46c), presumably because it is too bulky to enter the coordination sphere of the metal. A mechanism similar to that for the creation of (45) might thus be envisaged.

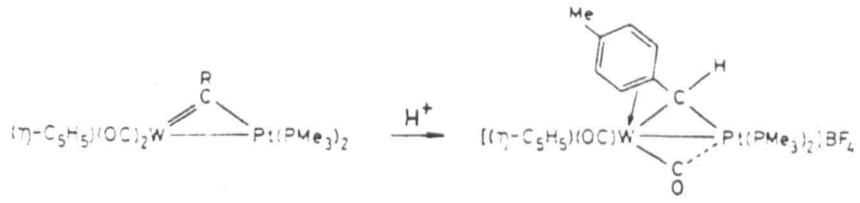


Alkynes have also been used by Stone et al. in the preparation of the hetero-dinuclear μ-allylidene (47) from the carbyne complex $[W(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CR)Co(CO)(\eta\text{-}C_5Me_5)]$, R = p-tolyl. Two steps are required for the synthesis of (47) from the carbyne; addition of but-2-yne and protonation. These may be carried out in either order, if protonation is first the intermediate formed is another μ-allylidene, which involves coordination of two of the tolyl ring carbons to attain the η^1,η^3 bonding mode.[63]



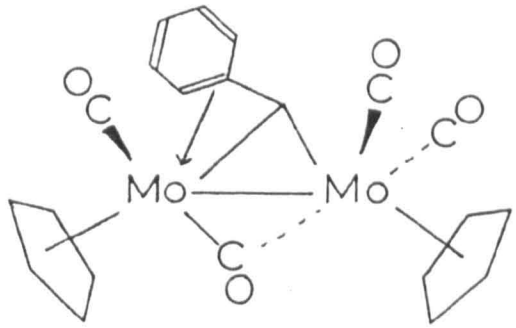
(47)

Bridging carbenes bearing aryl substituents have been shown to possess a similar η^1,η^3 mode of bonding in several other complexes. Another example from the Stone group is the tungsten-platinum species (48), again obtained by protonation of a μ-carbyne complex.[63]



(48)

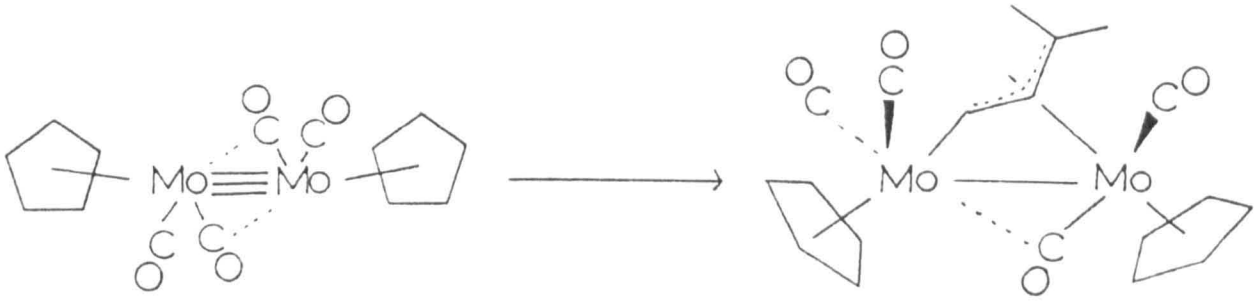
Curtis and Messerle have prepared $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\eta^1,\eta^3\text{-}CPh_2)]$ (49), from diphenyldiazomethane and $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$, the reaction proceeding via an intermediate in which CPh_2N_2 is coordinated.[64]



(49)

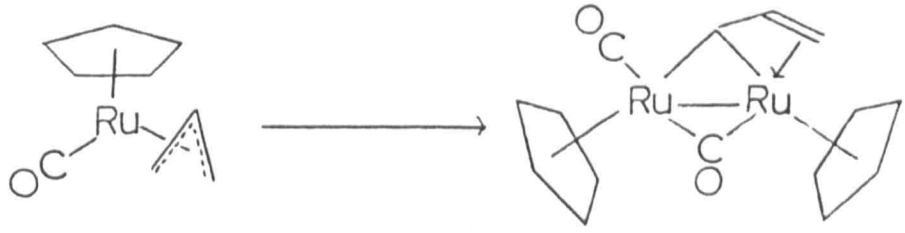
The same mode of bridging for CPh_2 is postulated by Knox et al. for $[Ru_2(\mu\text{-}CPh_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$ on the basis of n.m.r. evidence.[65]

Green and coworkers have observed the formation of a μ-allylidene complex analogous to (49) by addition of 3,3-dimethylcyclopropene to $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$.[66] The reaction proceeds by a C_1-C_3 ring-opening of the cyclopropene on the unsaturated molybenum dimer, the product (50) being a 1:1 adduct of the starting materials.



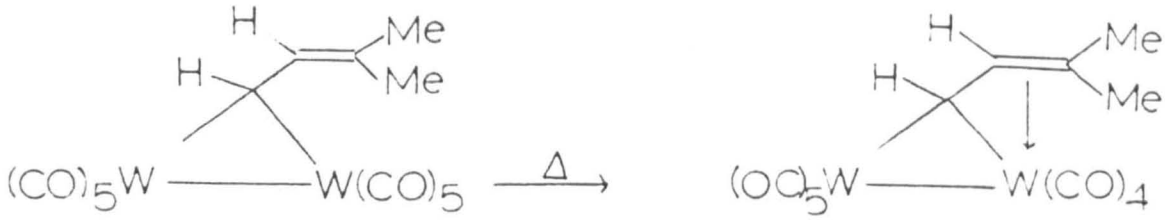
(50)

Together with the rational syntheses of μ-allylidene complexes there are also some rather serendipitous examples. Efraty et al. observed the transformation of the mononuclear π-allyl complexes (51) to the μ-allylidene species (52) in upwards of 40% maximum theoretical yield upon column chromatography.[67] The mechanism of the reaction is obscure and is likely to remain so due to the heterogeneous nature of the reaction conditions, however these findings do indicate a robustness of the μ-allylidene moiety which might not have been predicted due to its comparitive novelty.



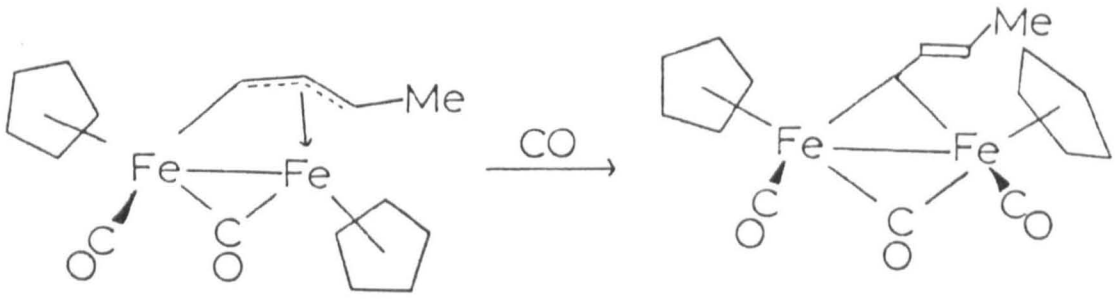
(51) (52)

The unusual formation of the complex (27), possessing a (μ-{η^1-vinylcarbene}) ligand has already been described. On standing in solution at room temperature this converted to the μ-allylidene (53) with evolution of carbon monoxide.[68]



(27) (53)

The reversibility of this last reaction is an important key to the reactivity of μ-allylidene complexes. Although Rudler did not report the reconversion of (53) back to (27) upon exposure to carbon monoxide, an analagous reaction has been observed by Knox et al. When (42) is subjected to 100 atm. of (CO) at 50°c for prolonged periods the μ-η^1-vinylcarbene (54) is produced.[60]



(42) (54)

The significance of this reaction lies in the fact that (27) had been produced from the μ-carbene complex [$Fe_2(\mu\text{-}CO)(\mu\text{-}CHMe)(CO)_2(\eta\text{-}C_5H_5)$]. The net chemical change over these two steps has been the

formal 'insertion' of an alkyne into the alkyl substituent of the carbene ligand, to produce a new carbene now bearing a vinyl substituent. This process of carbon chain lengthening might thus provide a mechanism for alkyne oligomerisation or polymerisation if the vinylcarbene complex formed displayed a similar reactivity to the starting alkylcarbene complex. Consequently the investigation of the chemistry of μ-allylidene complexes has centred on their reactions with acetylenes.

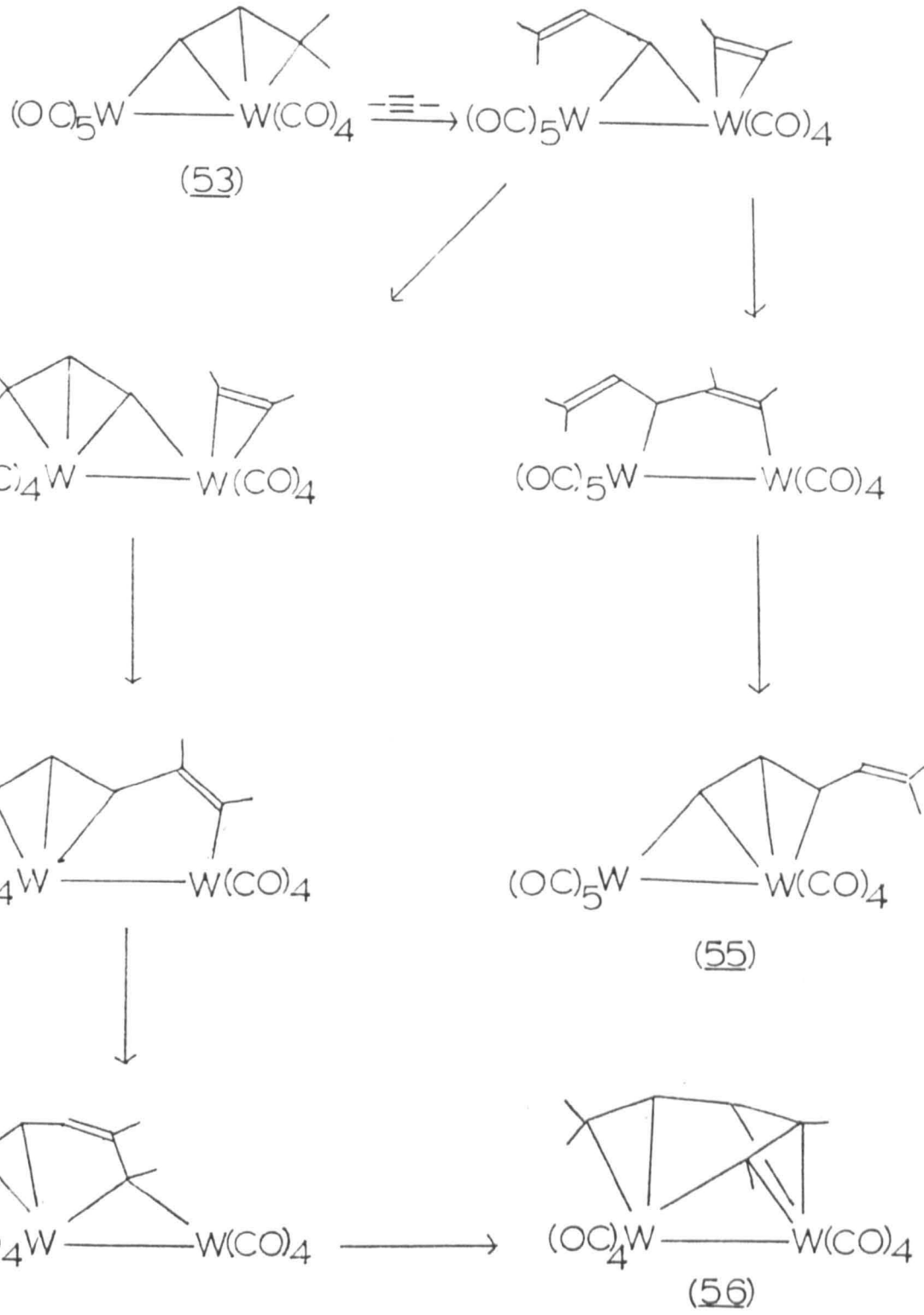
Rudler et al. have infact noted the formation of polymers in the reaction of (53) with 2-butyne.[69] Key intermediates in the chain lengthening process were also isolated and structurally characterised.[69,70] These are shown in Scheme 2.4, together with intermediates for the proposed mechanism.

The first step would be the conversion of the μ-allylidene into a μ-η^1-vinylcarbene and coordination of an alkyne ligand. This is reasonable based on the carbonylation reaction of (42), previously described, together with the isolation of phosphite adducts of (53), $[W_2(CO)_9L(\mu\text{-}\eta^1\text{-}CHCHCMe_2)]$, L = $P(OMe)_3$, $P(OEt)_3$, in which the μ-allylidene is similarly converted to a μ-η^1-vinylcarbene ligand.[71]

This would then be followed by insertion of the alkyne into the metal-carbene bond, to ultimately yield (55), or the 'wrap-around' complex (56) if decarbonylation additionally occurs.

These products (55) and (56), which are themselves both μ-allylidene complexes, may, in principle, continue the chain growth by their conversion to transient μ-η^1-vinylcarbene species allowing further alkyne uptake and insertion.

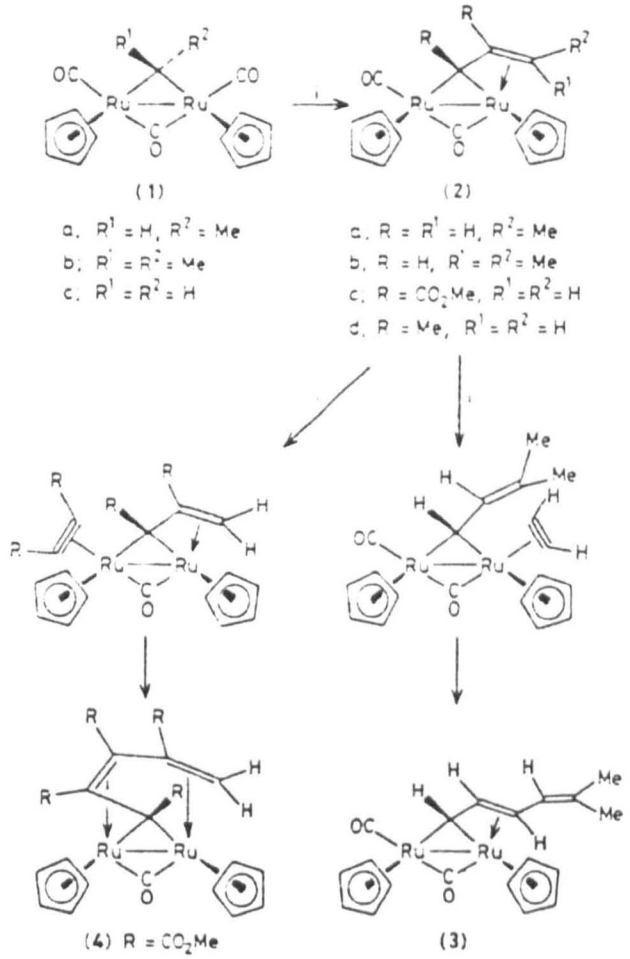
Scheme 2.4.


(OC)5W — W(CO)4
(53)
(OC)5W — W(CO)4
(OC)4W — W(CO)4
(OC)5W — W(CO)4
(CO)4W — W(CO)4
(OC)5W — W(CO)4
(55)
(OC)4W — W(CO)4
(OC)4W — W(CO)4
(56)

In practise, further insertion of 2-butyne into (55) occurs only at a very slow rate. Reaction of (53) with terminal alkynes leads however to much more rapid chain-growth and polymer formation.

The same ditungsten system has also been observed to effect the ring-opened polymerisation of cyclic olefins, for which a similar mechanism is proposed.[69]

Stereochemically controlled oligomerisation of alkynes has been reported by the Knox group for their diruthenium system.[72]



Reagents: i, u.v., −CO, RC_2R; ii, u.v., HC_2H.

Section 2.2

Results and Discussion

The following section describes seven crystal structures of various bi- and tri-metallic compounds resulting from the synthetic work of Dr. C.J. Schaverien and (in part) of Mr. R.J. Mercer of this Department.

The synthetic aims of the work were primarily to investigate the chemistry of the compound $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(\eta\text{-}C_5H_5)]$ with alkynes and other unsaturated hydrocarbons and to explore the reactivity of cyclopropenes towards bimetallic complexes which were either formally unsaturated or possessed potentially labile ligands.

Experimental details and complete spectroscopic data for the compounds described in this section may be found in the Ph.D. thesis of Dr. Schaverien[73] or the B.Sc. thesis of Mr. Mercer[74] and thus only brief descriptions of these will be given here by way of background to the crystallographic analyses.

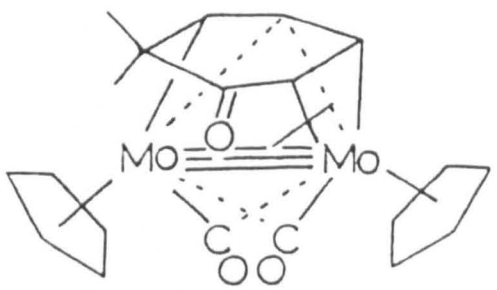
Reaction of $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(\eta\text{-}C_5H_5)_2]$ with Acetylenes

The potential of bridging allylidene complexes as alkyne polymerisation catalysts[75] prompted the investigation of the reaction of (50), $[Mo_2(CO)_4(CHCHCMe_2)(C_5H_5)_2]$ with acetylenes.

Accordingly, methylene chloride solutions of (50) were reacted with excess of various alkynes. Typically the reaction mixtures were heated in sealed vessels at 50°c for several hours, after which time the solvent was stripped off and the products separated by alumina chromatography.

3,3-Dimethylbut-1-yne

Two major products were isolated from this reaction. The complex (I) was afforded as dark green crystals in 20% yield. Its i.r. spectrum displayed absorptions at 1803, 1705 and 1595 cm^{-1}, the later being characteristic of a ketonic functionality. N.m.r. spectroscopy did not allow complete elucidation of the strucure of (I), though it appeared that one equivalent of $HC{\equiv}CBu^t$ had been incorporated into the molecule at the expense of a carbonyl group. One interesting feature of the ^1H n.m.r. spectrum was a second order ABX spin system, arising from single proton resonances at 5.20, 4.33 and 4.13 ppm . The $^{13}C(^1H)$ n.m.r. spectrum indicated that these protons belonged to a coordinated -CH.CH.CH- fragment.



(I)

Crystals of (I) grown from a CH_2Cl_2 / Et_2O mixture by layer diffusion were found to be of sufficient quality to allow a successful x-ray structure determination; refinement was to R = 0.0308, with the location of all atoms, including hydrogens. This showed (I) to be the dimolybdenum complex $[Mo_2(CO)_2(\mu\text{-}\{\eta^4\text{-}CMe_2.CH.CH.CH.C(Bu^t)CO\})(\eta\text{-}C_5H_5)_2]$, the molecular geometry and labelling scheme of which is shown in Figure 2.7.

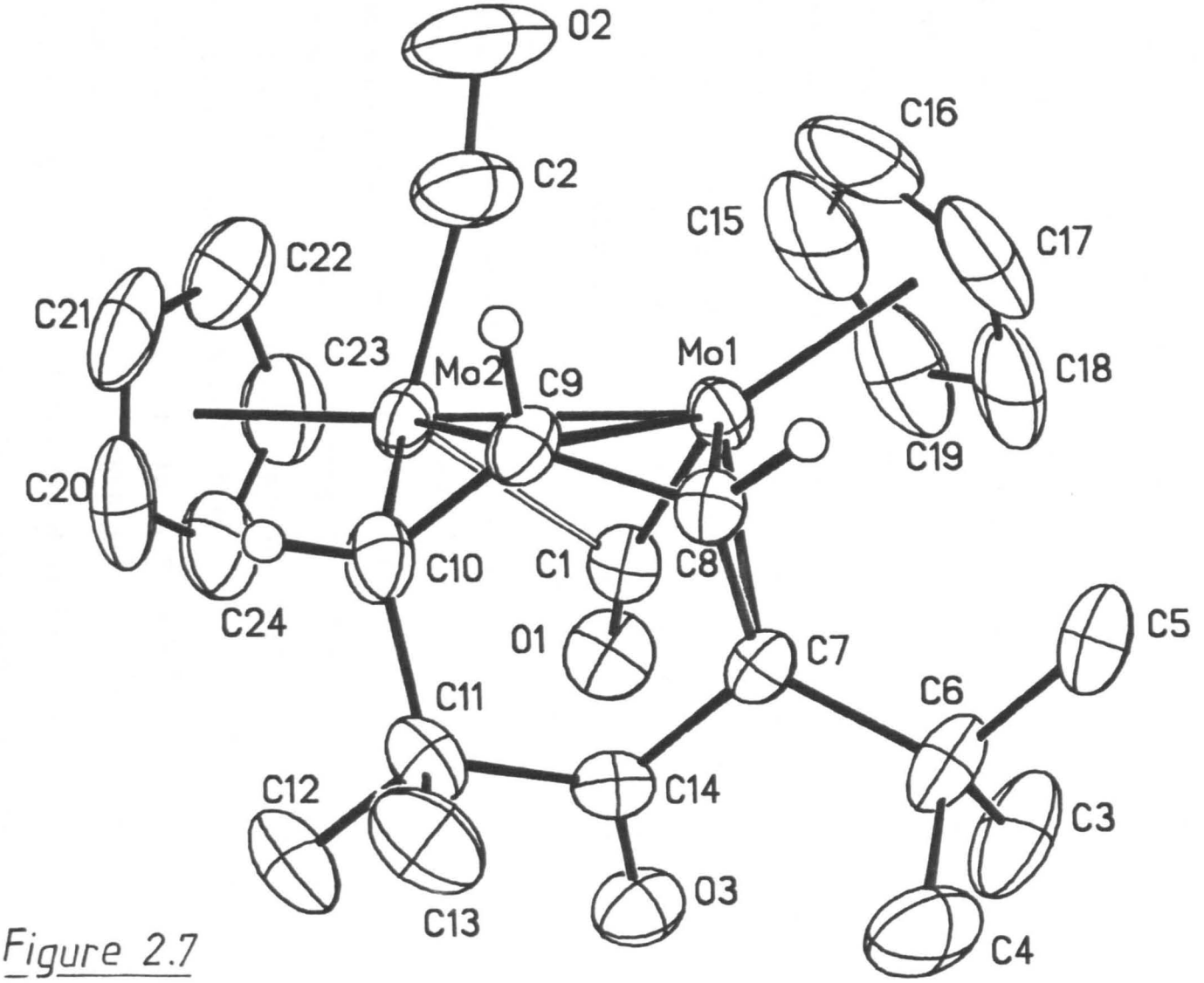

O2
C2
C16
C15
C17
C22
C21
C23
Mo2
C9
Mo1
C18
C19
C20
C10
C1
C8
C24
O1
C7
C5
C11
C6
C12
C14
C3
O3
C13
C4

Figure 2.7

Compound (I) consists of a $[Mo(\eta\text{-}C_5H_5)]_2$ core asymmetrically bridged by two carbonyl ligands and 2-^{t}butyl-6,6-dimethylcyclohexa-2,4-dieneone. Several features of (I) are structurally interesting. Firstly the dimolybdenum unit has a valence electron count of 30, six short of the number required by the EAN rule. This may be satisfied by a formal metal-metal triple bond.

The Mo(1)-Mo(2) internuclear separation in (I) is 2.524(1)Å, which may be compared with those of 2.448(1)Å in $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$,[76] 2.504(1)Å in $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)]$,[77] 2.488(3)Å in $[Mo(CO)_2(\eta\text{-}C_5Me_5)]_2$,[78] and 2.507(1)Å in $[Mo(CO)_2(HBpz_3)]_2$.[79] All of the above are dimolybdenum complexes with formal metal-metal triple bonds and which possess bridging ligands. Compound (I) would appear to fall into this category too, on the basis of its Mo-Mo 'bond length'.

Both of the carbonyl ligands in (I) show a degree of semi-bridging character, displaying significant deviation from linearity- Mo(1)-C(1)-O(1) = 163.2(5)°, Mo(2)-C(2)-O(2) = 168.4(7)°. Distances to the metals are asymmetric; Mo(1)-C(1) = 1.951(4)A, Mo(2)-C(1) = 2.335(5)Å and Mo(1)-C(2) = 2.654(5)Å, Mo(2)-C(2) = 1.918(6)Å. All of the above structural parameters point to the fact that carbonyl C(1)-O(1) has a greater degree of bridging character than C(2)-O(2).

That the carbonyl bridges are not totally compensatory is probably due to the unusual asymmetric bonding of the the diene ligand to the dimolybdenum unit. Typically in $\mu,\text{-}\eta^4$-cis-1,3-diene complexes, for example, $[Rh_2(\mu\text{-}\eta^4\text{-}CH_2CHCHCHCH_2)(\mu\text{-}CO)(\eta^5\text{-}C_9H_7)_2]$,[80] the metal atoms each bond to just two of the diene carbons such that two distinct metal-olefin interactions may be identified. In (I), however, one of the diene carbon atoms, C(9), is equidistant from Mo(1) and Mo(2), at 2.53Å,

and is apparently penta-coordinate. A valence bond description of the bonding of the diene to the metals is thus rendered difficult. Considerable delocalisation is found over the four carbon unit, as the C-C bond lengths show little variation; C(7)-C(8) = 1.439(5)Å, C(8)-C(9) = 1.428(7)Å and C(9)-C(10) = 1.470(6)Å. The greater share of the metal-diene bonding involves Mo(1), which is bound to C(7) and C(8) at distances of 2.396(4)Å and 2.222(4)Å respectively. Mo(2) is bonded to C(10) at a distance of 2.232(5)Å.

The origin of the asymmetry in the diene bonding found in (I) is probably the relief of unfavorable steric interactions. The bulk of the ^{t}butyl substituent on C(7) may prevent the attainment of the diene geometry observed in the dirhodium complex, in which the central C-C bond lies parallel to the metal-metal vector. In (I), this orientation would lead to unfavorable interactions between the hydrogen atoms on C(5) of the ^{t}butyl group and C(17) of the cyclopentadienyl ring bound to Mo(1). The avoidance of this in (I), may be effected by what can be described as a rotation of the diene by 23.3° in a plane parallel to the metals as shown in Fig 2.8. The effect of this is to 'tip' the diene towards Mo(1) and away from Mo(2).

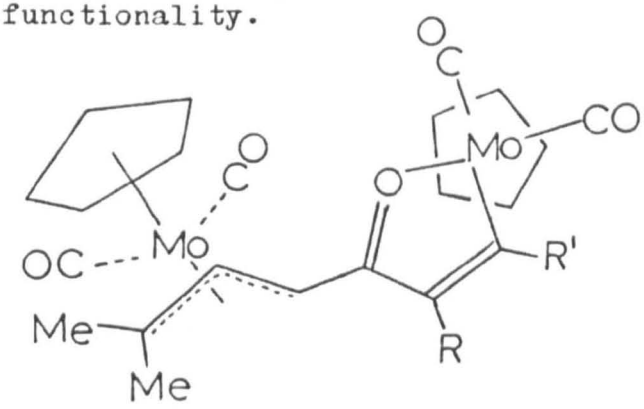
Fig 2.8. Orientation of bridging diene ligands

The C(7)-C(10) unit is planar (no deviation from the l.s. plane by more than 0.05Å). The ketone function of the cyclohexadienone ligand also lies roughly in this plane perhaps allowing a certain degree of π-conjugation. The ketonic bond length C(14)-O(3) of 1.207(4)Å, is in the range expected;[81] the other bond lengths and angles for the complex are unremarkable.

The second major product from the reaction of ^{t}-butylacetylene with (50) was a deep red crystalline complex (57) which was obtained in 40% yield. The structural identity of this compound was established by comparison of its n.m.r. parameters with its analogue (II), the only product isolated (50%) from the reaction of (50) with 2-butyne.

2-Butyne

Crystals of the compound (II) suitable for a single crystal x-ray diffraction study were obtained from a CH_2Cl_2/hexane mixture. As in the case of (I), a structure determination was deemed necessary as a conclusive formulation could not be obtained from the spectroscopic data. Compound (II) showed two terminal $\nu_{(CO)}$ bands at 1940 and 1865 cm^{-1} and another absorption at 1605cm^{-1}. This latter was assumed to arise from a keto- functionality.



(57)
R = H R' = Bu^t

(II)
R = R' = Me

The n.m.r. data for (57) indicated that it had resulted from the addition of an equivalent of ^{t}butylacetylene and one carbon monoxide moiety to (50); four terminal carbonyl ^{13}C n.m.r. resonances were observed between 253.7 and 238.2 ppm. The low field region of the spectrum also showed a peak at 274.2 ppm, which was thought to be carbenoid in nature, together with a resonance at 201.4 ppm, characteristic of a ketonic carbon. Once the accidental equivalence of certain peaks in the ^{13}C n.m.r. spectrum of (II) had been identified, it became obvious that this compound also possessed five carbonyl moieties and was structurally analogous to (57).

This was confirmed by the results of the x-ray diffraction study of (II). Its molecular structure, with atomic labelling scheme, is shown in Figure 2.9. Compound (II) is a dinuclear molybdenum complex with no direct metal-metal bond. It consists of two $[Mo(CO)_2(C_5H_5)]$ units spanned by a ligand binding as an exo-η^3-allyl to one metal and as a η^2-vinylketone to the other.

The loss of the Mo-Mo bond was revealed at an early stage of the structure determination, as the shortest metal-metal vector observed in the Patterson map had a magnitude of 5.8Å. Refinement of the structure proceeded smoothly, yielding a final R of 0.031 and allowing the location of all atoms.

As in the case of (I), a complex ligand had been formed from a 'condensation' of alkyne, CO and μ-allylidene moieties. In (II), the coordination sphere of Mo(2) is completed by a η^3-allyl group which is obviously derived from the original μ-allylidene fragment of the starting material (50).

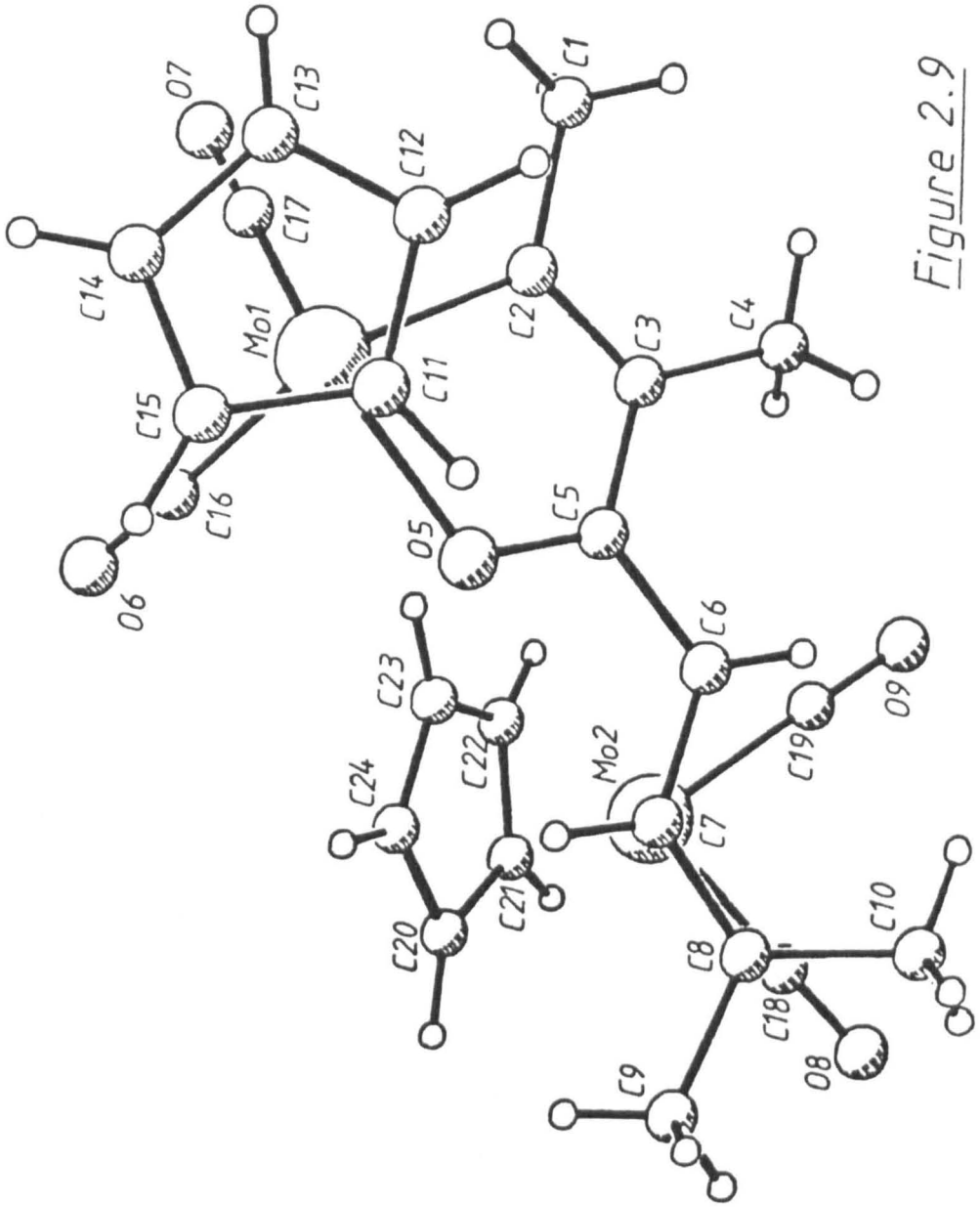
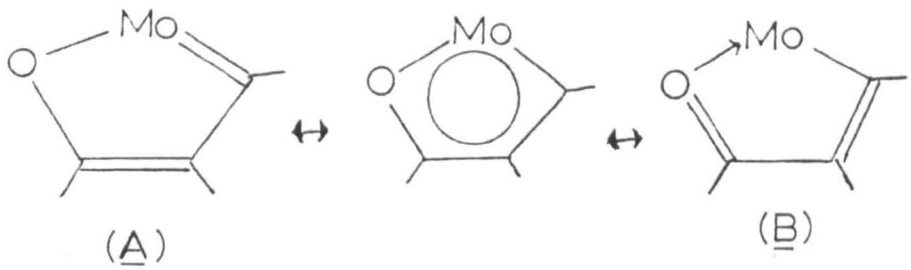

O7
C13
C1
C12
C17
C14
C2
Mo1
C3
C4
C11
C15
C16
O5
C5
O6
C6
C23
O9
C19
C22
Mo2
C24
C7
C21
C10
C20
C8
C18
O8
C9

Figure 2.9

(II)

The allyl function is bound in an exo- fashion; the central carbon atom is more tightly bound to the metal than the two outer ones - Mo(2)-C(7) = 2.239(4)Å compared to Mo(2)-C(6) = 2.349(4)Å and Mo(2)-C(8) = 2.463(4)Å. The allyl is substituted in the Syn -position of C(6) by the keto-carbon, C(5), of the η^2-vinylketone which is bonded to Mo(1), forming a delocalised molybdacyclopentenone ring. This may be thought of as a hybrid of the two canonical forms shown in Figure 2.10.



(A) (B)

Figure 2.10.

The Mo(1)-C(2) distance of 2.158(4)Å lies between that expected for molybdenum-carbon double and single bonds. The Mo(1)-O(5) bond of 2.132(5)Å is shorter than the Mo-O bond of 2.212(2)Å found for $[Mo_2(CO)_4(OCOCF_3)(C_5H_5)_2(\mu\text{-}CHCH_2)]$.[82] This suggests that there is considerable π-bonding between these two atoms. The C-C bond lengths of 1.378(6)Å and 1.420(5)Å for C(2)-C(3) and C(3)-C(5) respectively, give an indication that canonical form B is predominant. The value of 1.286(4)Å for the C(5)-O(5) bond is considerably longer than that of 1.207(4)Å found for the unbound keto- function in (I), however. The structural parameters for the vinylketone group in (II) may be compared with those obtained for the mononuclear molybdenum complex (58), $[Mo(CO)_2(\eta^2\text{-}CMeCMeC\{CMeCHMe\}O)(C_5H_5)]$.[83] (Table 2.1).

Bond (Å)	(II)	(58)
Mo — O	2.132(5)	2.110(3)
Mo — C1	2.158(4)	2.142(3)
C1 — C2	1.378(6)	1.380(4)
C2 — C3	1.420(5)	1.416(4)
C3 — O	1.286(4)	1.292(4)

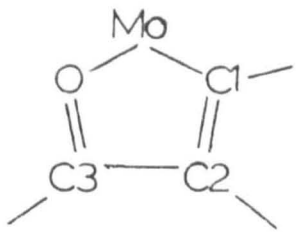


Table 2.1.

No particularly significant differences are observed.

1,2-(Methylcarboxy)ethyne

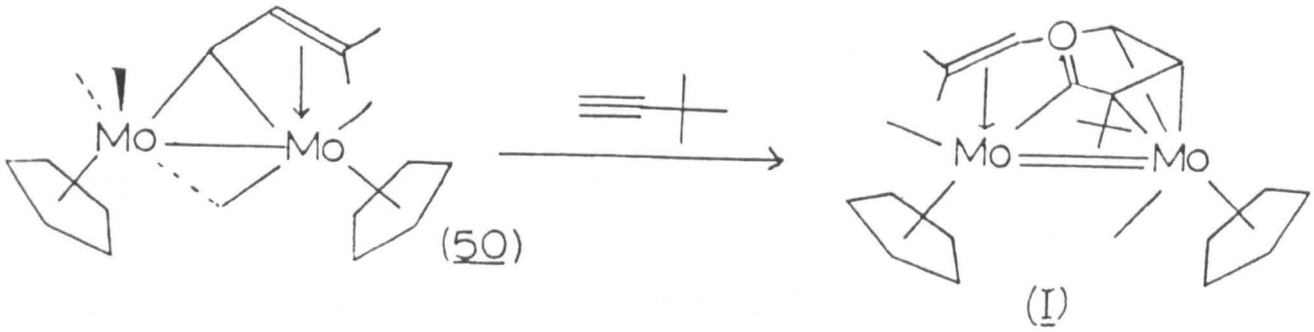
Reaction of the μ-allylidene complex (50) with the electron poor alkyne [$C_2(CO_2Me)_2$] at 50°c for 3 hr was found to yield one isolable product in 40% yield. This was the red crystalline complex (59). This was analogous to neither (I) or (II), but on the basis of spectroscopic evidence shown to have the form given in Scheme 2.6. In this compound the alkyne has inserted into the metal-carbene bond of the μ-allylidene. This type of reaction had been previously observed in Fe_2, Ru_2 and W_2 chemistry.[60,69,84]

Mechanism of Formation of (I) and (II)

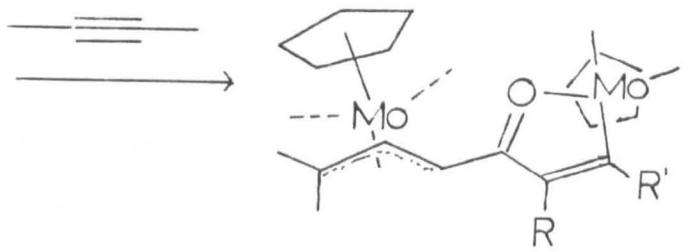
The results of alkyne addition to the μ-allylidene complex (50) indicate that several reaction pathways are possible for this system in addition to the chain extension mechanism which was previously discussed for the ditungsten system of Rudler et al.

It would appear that subtle electronic or steric factors are at work in deciding which pathway is favoured by a particular alkyne. Whilst

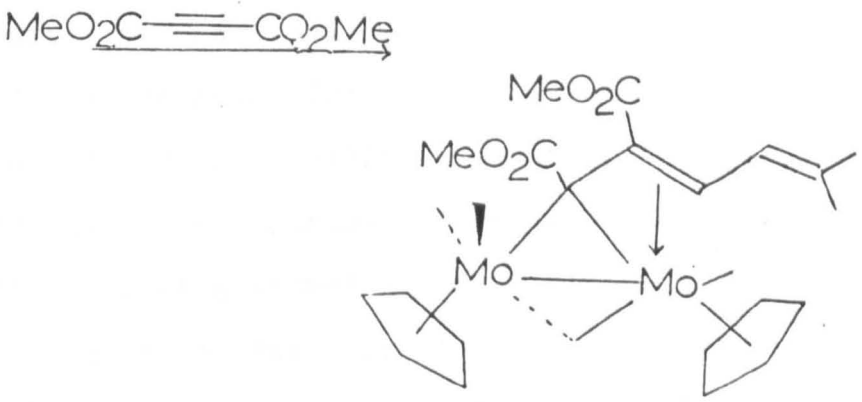
Scheme 2.6 The Reactions of the μ-allylidene complex $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(C_5H_5)_2]$ with Acetylenes.



(50) (I)



(II) R=R'=Me
R=H, R'=Bu^t



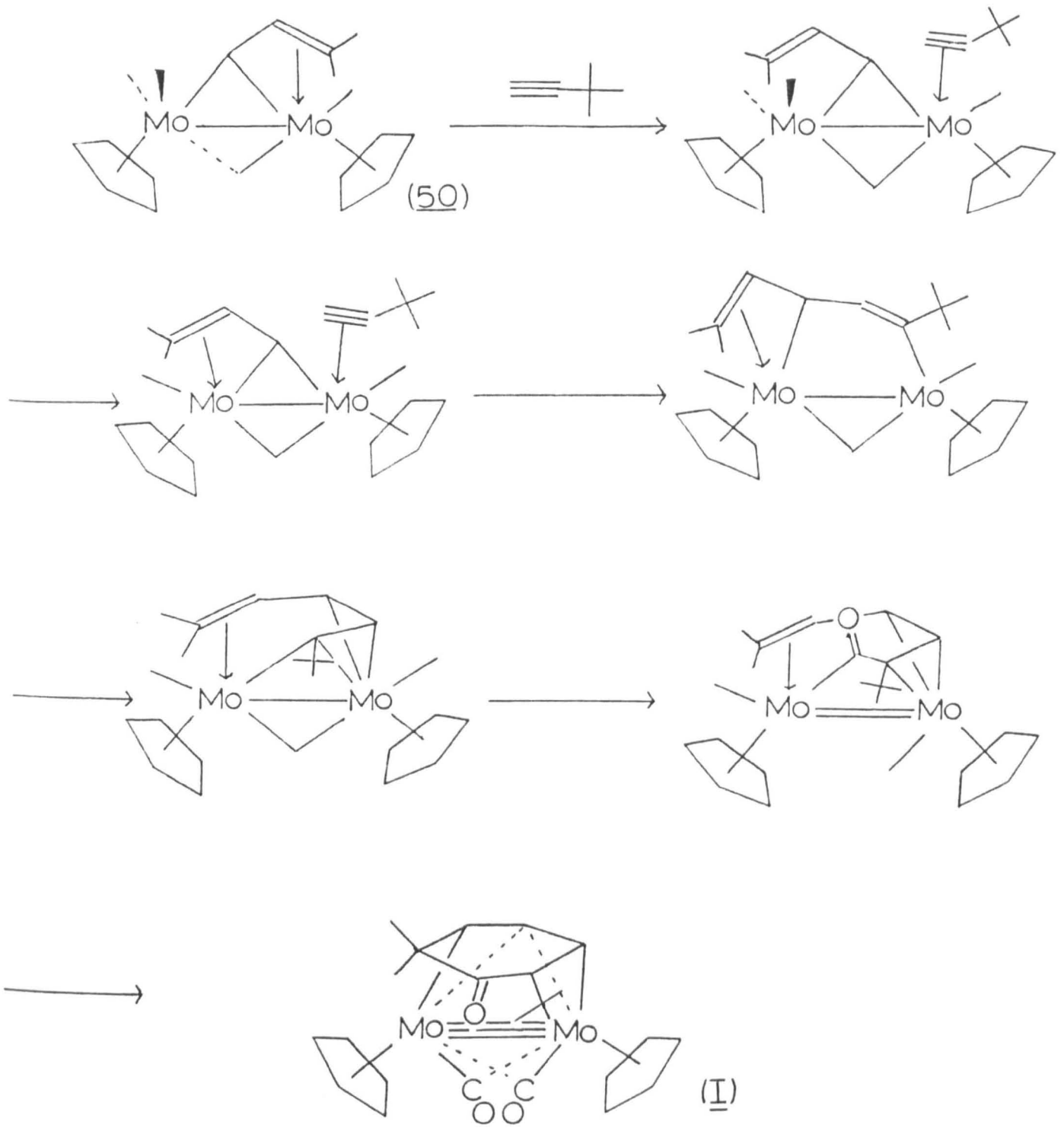
these factors may not be readily apparent, plausible mechanisms for the formation of (I), (II) and analogous products may be proposed.

The formation of (I) requires the net replacement of a carbon monoxide ligand by one equivalent of alkyne. A possible way for this substitution to occur is outlined in Scheme 2.7. Steps (1) and (2) account for the exchange of a (CO) for an acetylene. Similar steps were originally proposed by Rudler for substitution of carbonyls by acetylenes and phosphines in the complex $[W_2(CO)_9(\mu\text{-}CHCHCMe_2)]$.[69,71] Steps (3) and (4) also follow Rudler's scheme for the formation of (55). All that is then required is a carbonyl insertion into one of the μ-carbene bonds, followed by a reductive elimination step which effects cyclohexadienone formation. These last two operations successively reduce the valence electron count at the dimetal centre which is represented in the scheme by an increase in the formal Mo-Mo bond order.

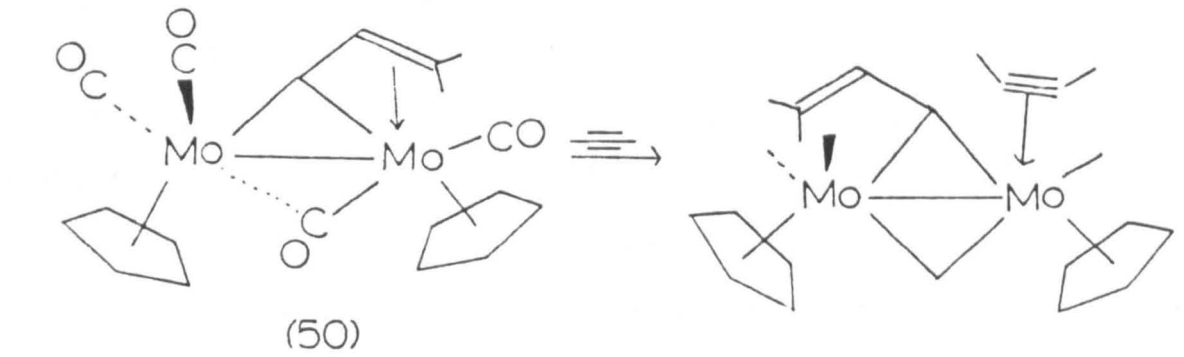
Formation of (II) (and its analogue (57)) requires not only addition of an equivalent of alkyne but also the scavenging of a molecule of carbon monoxide. This may be provided by either decomposition of the starting material or reactions involving (CO) evolution as in the formation of (I). All of the reactions were carried out in sealed tubes thus free carbon monoxide was not lost from the reaction system.

Scheme 2.8 outlines a mechanism for the formation of (II) and its analogue (57). The initial steps probably involve the ligand additions, the second being accomodated by a carbonyl insertion. The organic skeleton of the complex bridging ligand found in (II) may then be obtained *via* a second insertion, this time involving the acyl and acetylene moieties. The final step shows metal-metal bond rupture and $\eta^1\text{-}\eta^3$ allyl and $\eta^1\text{-}\eta^2$ vinylketone conversions.

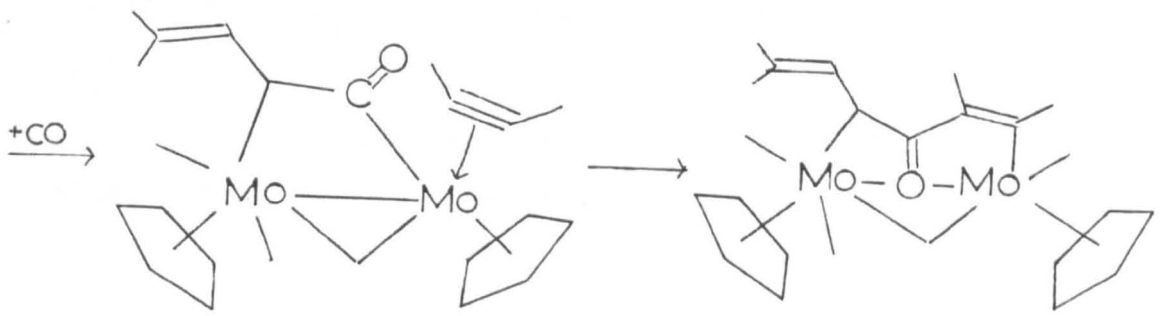
Scheme 2.7. Mechanism of Formation of (I)

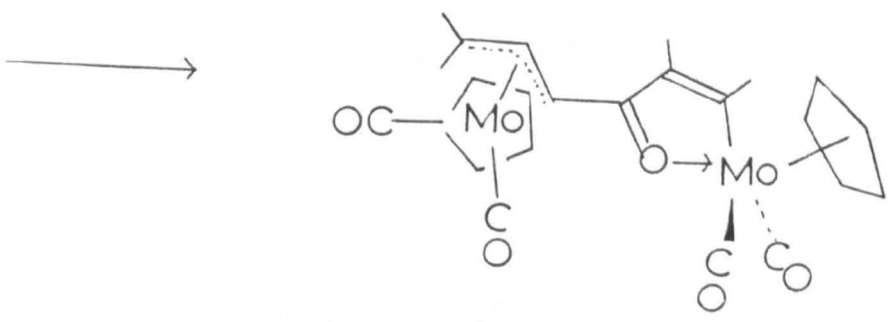


Scheme 2.8. Mechanism of Formation of (II)



(50)





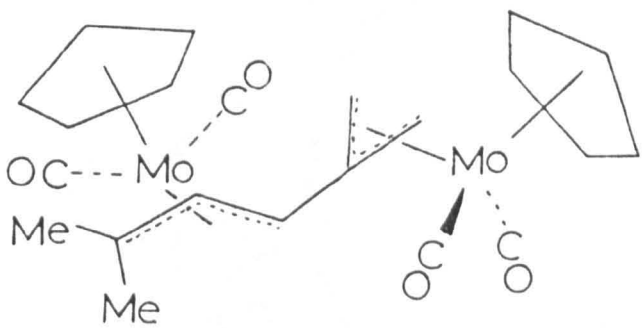
(II)

Reaction of the μ-Allylidene Complex $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(C_5H_5)_2]$ with other Unsaturated Hydrocarbons

Allenes

The rich chemistry of the μ-allylidene complex (50) with alkynes indicated that it should also be reactive towards other highly unsaturated hydrocarbon molecules. It had already been observed to react further with 3,3-dimethylcyclopropene although the products were either too fragile or intractable to allow their characterisation.[85] The reaction of (50) with both allene and dimethylallene was carried out in a similar way to the acetylene reactions.[74]

The product from the allene reaction was recrystallised from hexane to yield deep orange prisms of (III). The spectroscopic data on this compound indicated that it was a 1:1 adduct of the reactants. In order to clarify the nature of (III) a structure determination was undertaken.



(III)

The results show that (III), like (II), is a dimolybdenum complex in which the two coordination spheres of the metals are discrete. The molecular structure, with atom labelling scheme is given in Figures 2.11 and 2.12.

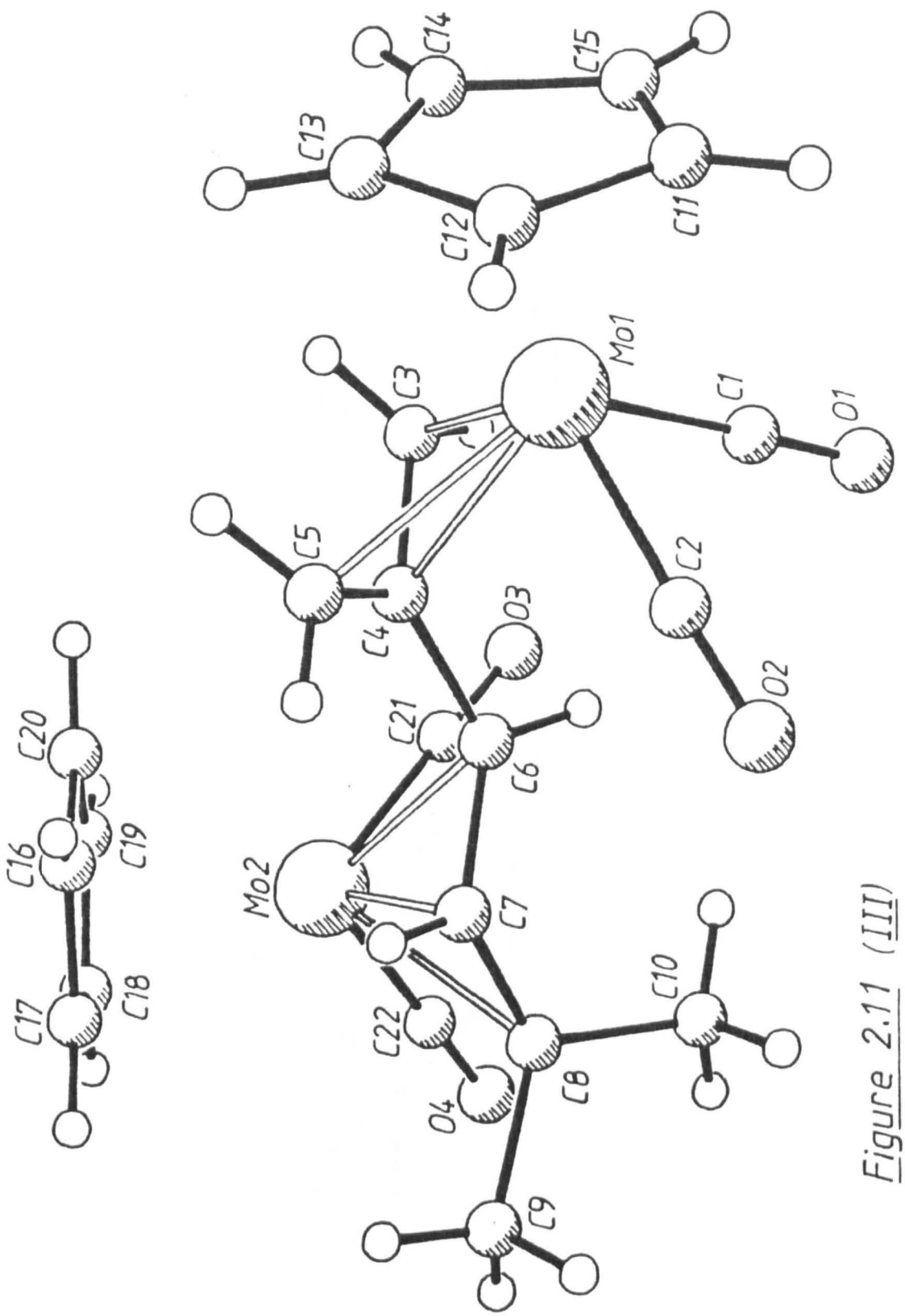
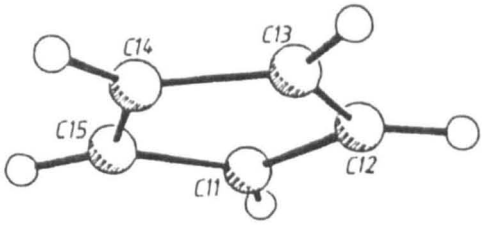
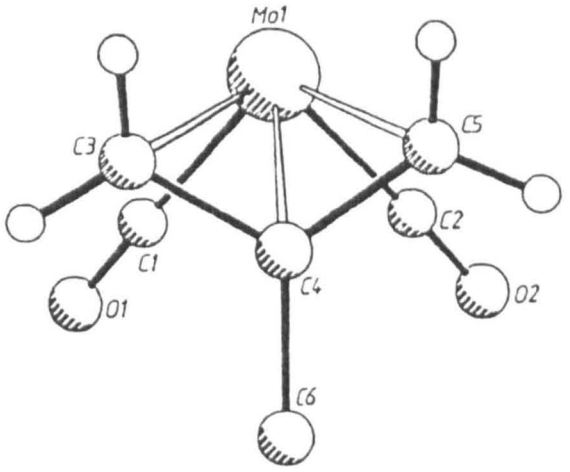
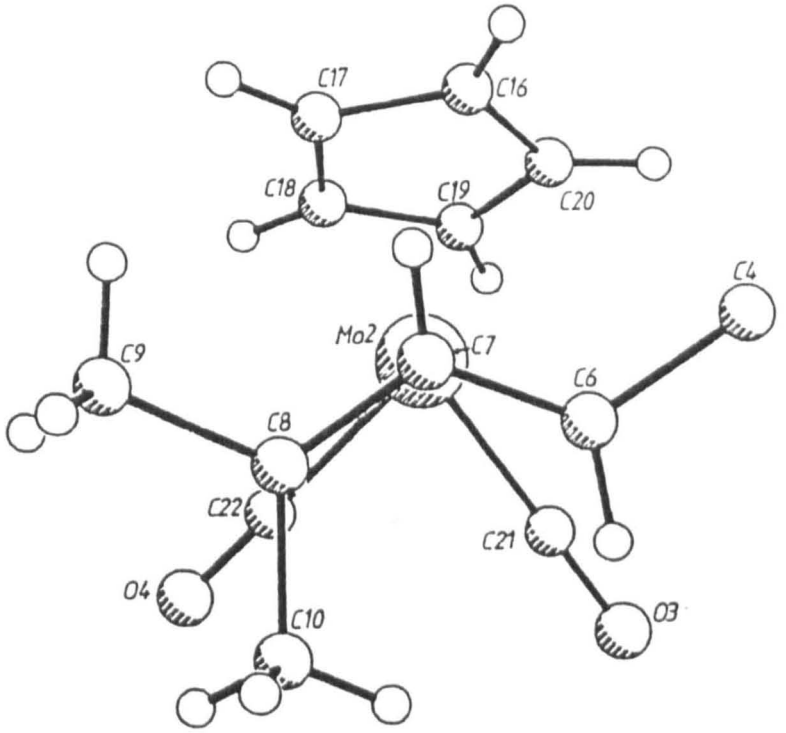


Figure 2.11 (III)


C14
C13
C15
C12
C11


Mo1
C3
C5
C2
C1
C4
O2
O1
C6


C17
C16
C18
C19
C20
C4
Mo2
C7
C9
C6
C8
C22
C21
O4
O3
C10

The complex may be descibed as two cyclopentadienyl molybdenum cis-dicarbonyl units spanned by a complex organic ligand formed from addition of allene to thhe original μ-allylidene moiety. This acts as a η^3-endo π-allyl ligand to Mo(1) and a η^3-exo π-allyl to Mo(2). The two allylic functionalities are directly joined by a C-C bond from C(4), the central carbon of the endo- component to the Syn position of C(6), one of the outer carbons of the exo- allyl fragment.

The structure of (III) allows a direct comparison of the geometries of exo- and endo- π-allyl ligands. As was observed in (II), the central carbon in the exo- conformation is closer to the metal than the outer pair. In this case Mo(2)-C(7) = 2.238(3)Å compared with Mo(2)-C(6) = 2.356(2)Å and Mo(2)-C(8) = 2.428(2)Å. In contrast the endo- configuration sees the outer pair in closer contact with the metal, as indicated by Mo(1)-C(3), Mo(1)-C(5) = 2.290, 2.318(3)Å and Mo(1)-C(4) = 2.325(3)Å. The angles subtended by the allyl moieties at the molybdenum centres (i.e. the ligand bite angle) are quite similar, being 62.3° for the exo and 62.0°(1) for the endo configurations respectively.

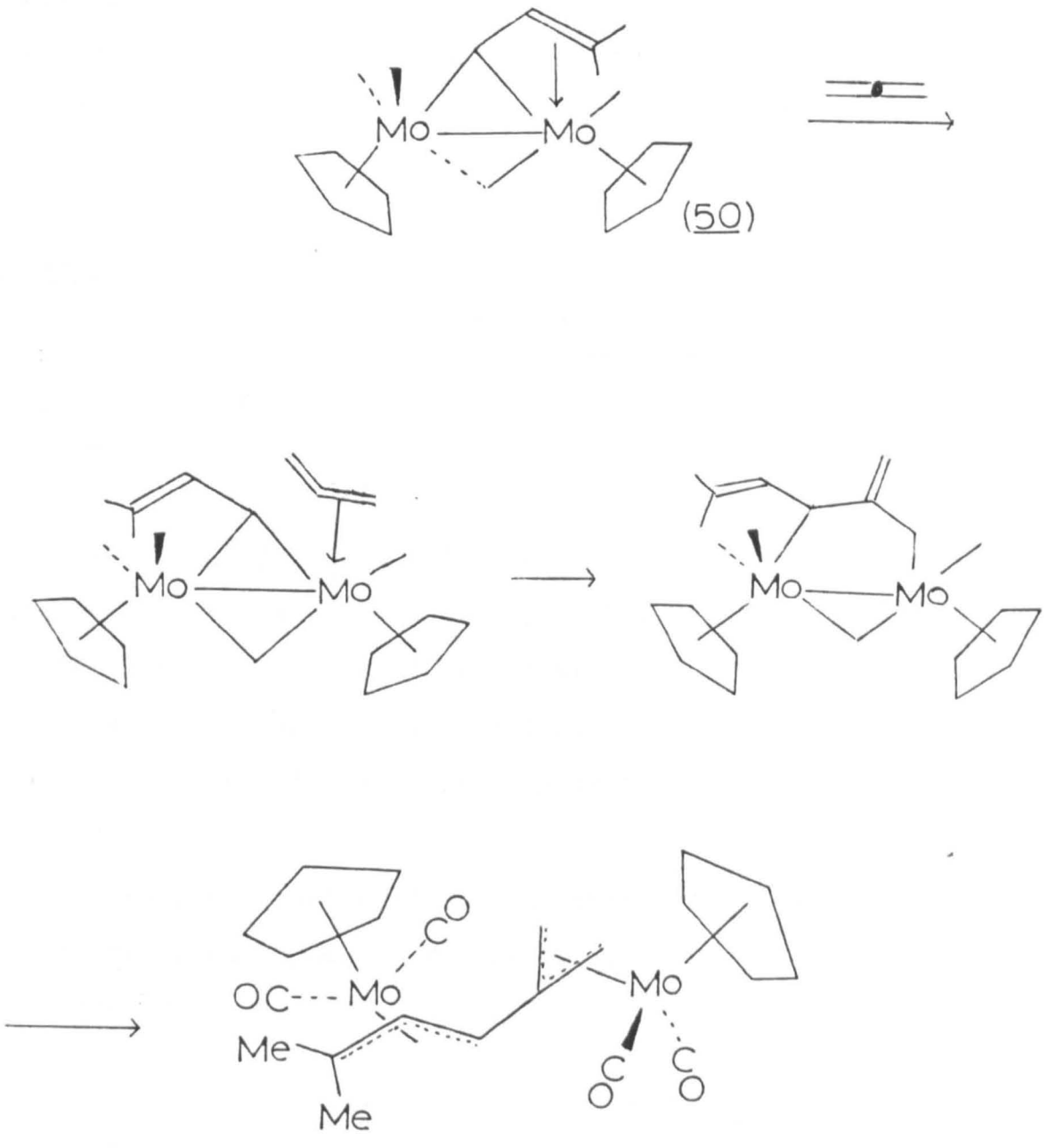
Mechanism of Formation of (III)

The formation of (III) differs from both that of (I) or (II), in that addition, loss or insertion of the carbonyl groups do not take place. The first step may once more be thought of as conversion of the μ-allylidene to a η^1-vinylcarbene which would allow coordination of the allene. A carbon-carbon bond formation then takes place (i.e. reductive elimination at Mo(1)). The species thus formed would essentially be (III). (Scheme 2.9).

Table 2.2 Geometry of Molybdenum π-Allyl Complexes

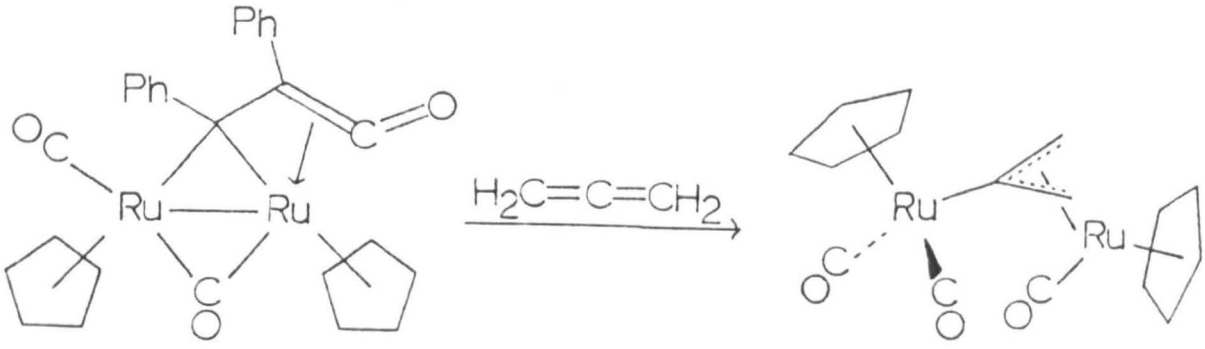
Compound	$M-C_{inner}$	$M-C_{outer}$	Bite Angle	Ref.
$[Mo_2(CO)_4(\mu\text{-}CMe_2CHCHCOCMeCMe)(\eta\text{-}C_5H_5)_2]$ (II) (exo-)	2.239(4)	2.349(4) 2.463(4)		This work
$[Mo_2(CO)_4\{\mu\text{-}CMe_2CHCHC(CH)_2\}(\eta\text{-}C_5H_5)_2]$ (III) (exo- and endo-)	2.238(3)	2.356( ) 2.428(2)	62.3	This work
	2.325(3)	2.290(3) 2.315(3)	62.0	
$[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ exo	2.236(4)	2.359(3) 2.359(3)	61.3(2)°	86a
$[Mo(CO)_2(\eta\text{-}C_3H_5)\{PPh_2(CH_2)_2PPh_2\}Cl]$	2.221(12)	2.340(12) 2.350(17)	60.5(5)	86b
$[Mo(NO)(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_4R)I]$ R = neomenthyl endo	2.27(1)	2.343(8) 2.42(1)		86c
$[Mo(CO)(NO)(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_4R)]$ R = neomenthyl endo	2.333(10)	2.357(7) 2.396(8)		86c
$[Mo(CO)_2\{P(OMe)_3\}_2(\eta\text{-}C_3H_5)Cl]$	2.35(2)	2.40(2) 2.40(2)	61.2(8)	87

Scheme 2.9. Mechanism of the Formation of (III)



(III)

It is interesting to compare the reaction of (50) with allene to that of the diruthenium complex $[Ru_2(CO)_2(\mu\text{-}CPhCPhO)(C_5H_5)_2]$, (60), which is formed upon irradiation of $[Ru(CO)_2(C_5H_5)]_2$ with diphenylacetylene.[88] This may be thought of as a μ-allylidene analogue. However the reaction product, (61), is quite different from (III), in that a substitution, rather than an addition reaction has occured.[89]



(60) (61)

Conversion of (60) to (61) probably involves the reverse of the carbonyl insertion process by which (60) was formed, and replacement of the the μ-acetylene ligand by the allene. If this is true, (61) should be expected to form upon u.v. radiation of the $[Ru(CO)_2(C_5H_5)]_2$ dimer with allene. Indeed these replacement reactions occur very readily with (60).[65]

In order for μ-allylidenes to exhibit the same type of chemistry one of the two steps shown in Figure 2.13, invoving C-C bond cleavage would be necessary.

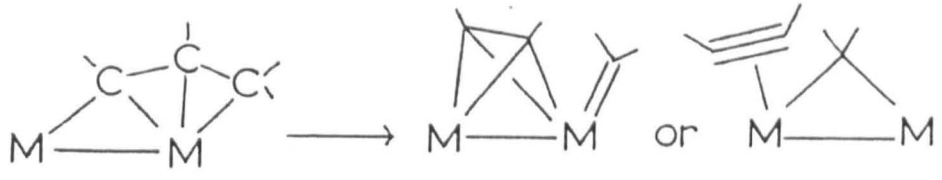
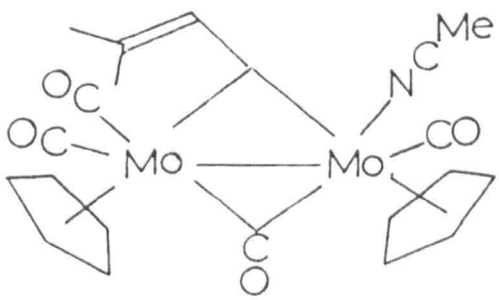


Figure 2.13

So far this behaviour has not been observed for μ-allylidenes, but rather (CO) substitution tends to occur as discussed for the ditungsten species of Rudler.

Hydrolysis of $[Mo_2(CO)_4(\mu\text{-}CHCHCMe_2)(C_5H_5)_2]$

The reaction of (50) with acetylenes was consistent with initial π-coordination of the alkyne to a vacant site on one of the metal centres created by μ-η^1,η^3-allylidene to μ-η^1-vinylcarbene conversion. It was hoped that in the presence of a donor ligand such as acetonitrile that it might prove possible to trap out such a μ-carbene complex (62).



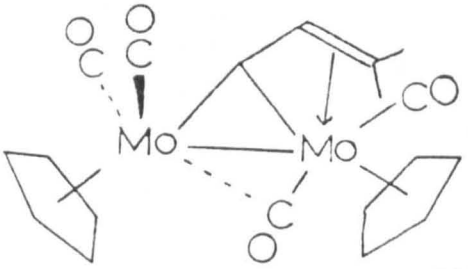
(62)

Isolation of (62) might prove synthetically desirable as the acetonitrile ligand would be expected to be labile and so allow access to a range of further compounds by ligand addition under mild conditions.

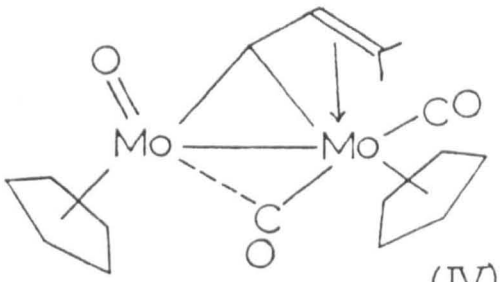
Complex (62) was not obtained upon refluxing an acetonitrile solution of (50), although changes in the infra red spectrum of the solution did indicate that a new compound (IV) had been formed.

The acetonitrile did not appear to have played any active role in the reaction, the n.m.r. spectra indicating the presence of two cyclopentadienyl groups, two carbonyl ligands and an apparently intact μ-allylidene unit. In view of this it was decided that a crystal structure analysis of (IV) would be of use in determining its relationship to (50).

The results showed that (IV) differed from (50) in the replacement of two terminal carbonyl groups by a terminal oxo ligand. The molecular geometry and labelling scheme for (IV) are given in Figures 2.14 and 2.15.



(50)



(IV)

The structure of (IV) may be readily compared with that previously determined for (50), both analyses being carried out at room temperature with data of reasonable quality. The final R value for (IV) was 0.0252, all atoms being located.

There are several significant structural changes between the two compounds. First the metal-metal internuclear separation is reduced from 3.106(1)Å found in (50) to 2.881(1)Å in (IV). The semi-bridging carbonyl ligand is much more symmetric in its bridging in (IV). The Mo-μC(O) distances of 1.990(7)Å and 2.473(7)Å in (50) correspond to values of 2.060(3)Å and 2.161(3)Å in (IV).

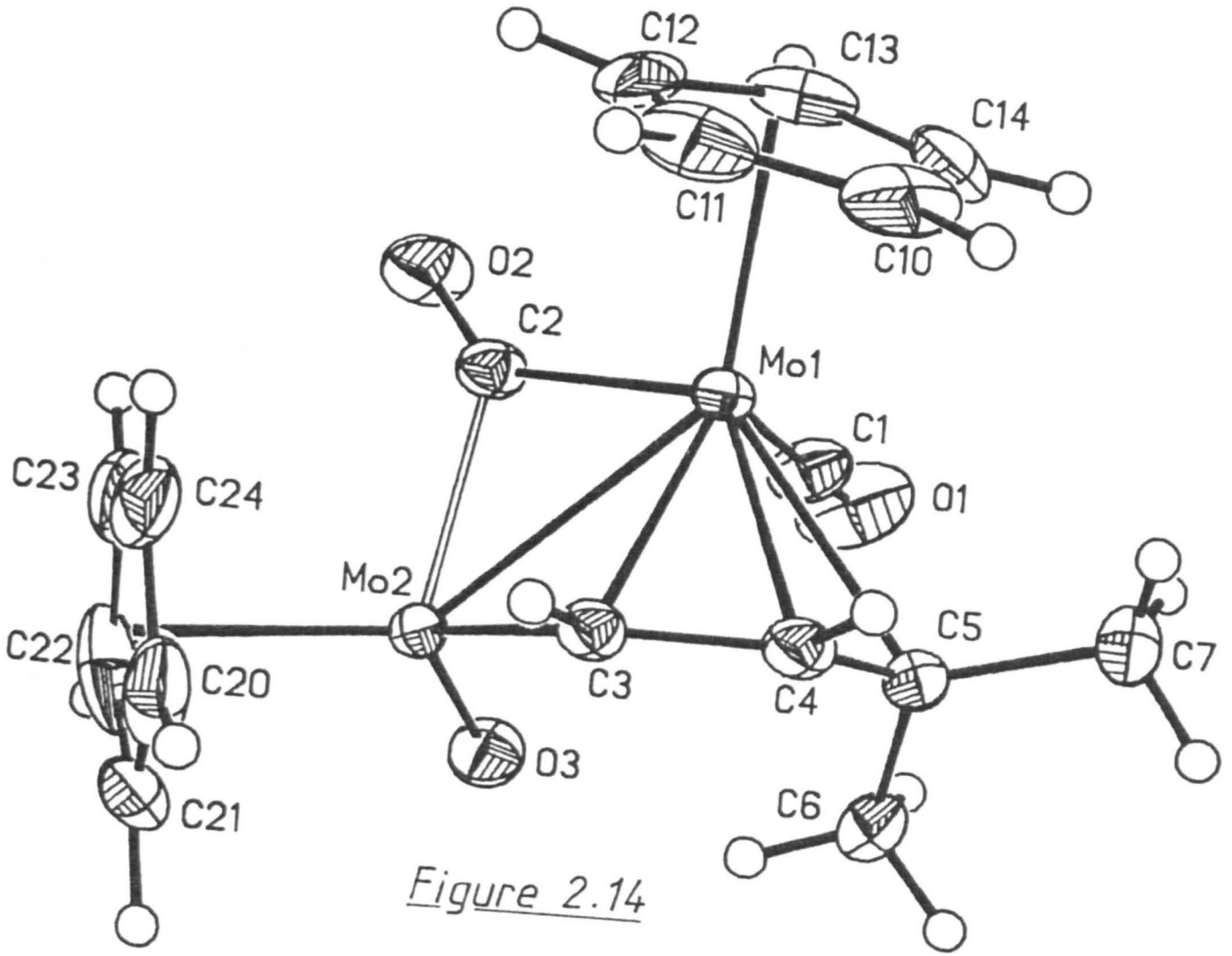

C12
C13
C14
C11
C10
O2
C2
Mo1
C1
O1
C23
C24
Mo2
C22
C20
C3
C4
C5
C7
O3
C21
C6

Figure 2.14

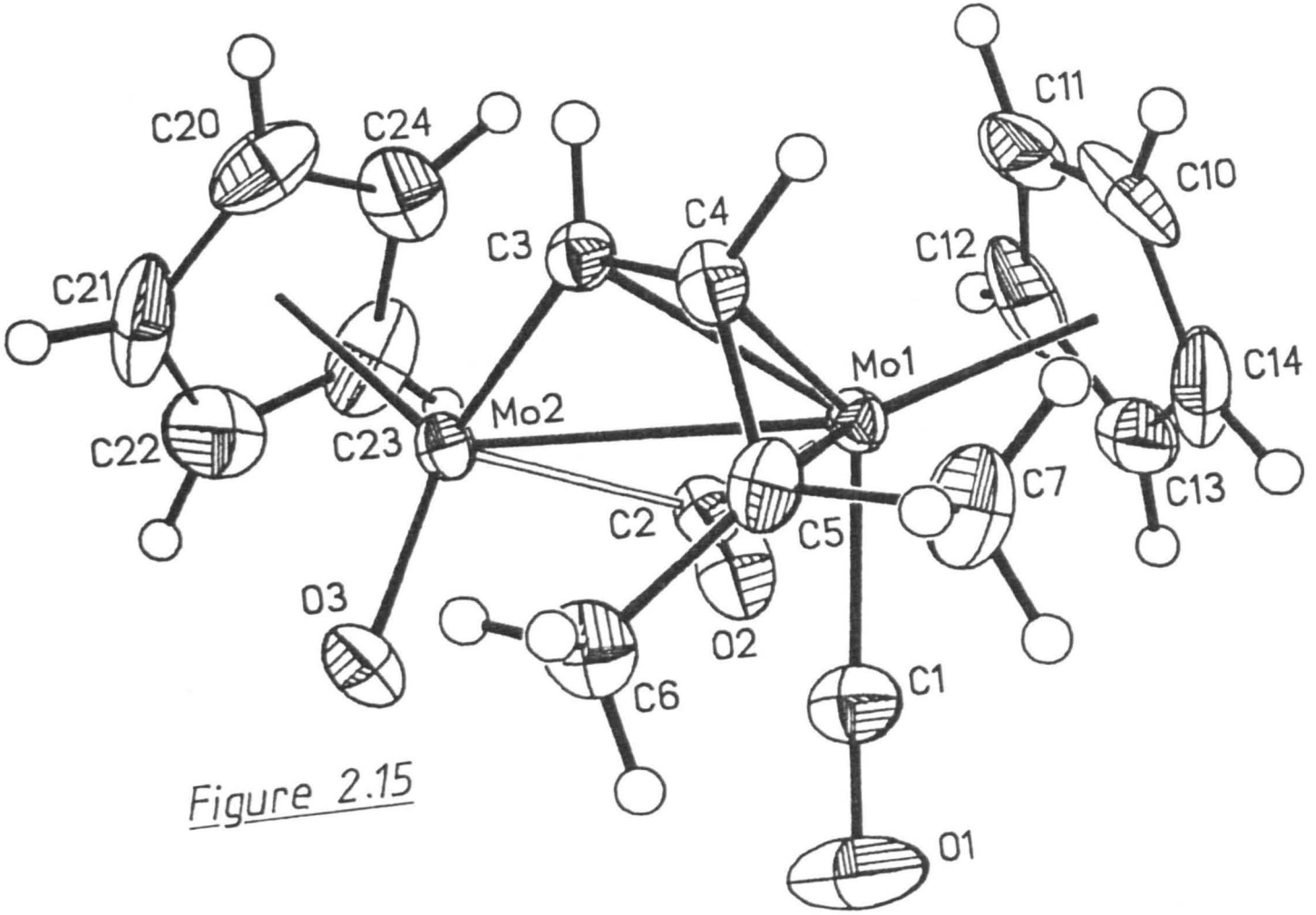

C20
C24
C21
C22
C23
C3
C4
C11
C10
C12
C14
Mo1
Mo2
C7
C13
C2
C5
O3
O2
C6
C1
O1

Figure 2.15

No major changes are found for the allylidene unit. The largest difference is found for the bridging carbon atom of the ligand, C(3), which is less symmetrically bound in (IV) than it was in (50).

Thus the bond to the molybdenum atom at which the two carbonyls have been exchanged for the oxo group is shorter in (IV) (Mo(2)-C(3) = 2.088(3)Å) than in (50) for which the corresponding length is 2.126(6)Å. There is less change in the bonding to Mo(1) as can be seen in the table comparing key bond lengths for the two structures. The main differences may be explained by consideration of π-bonding effects. Replacement of two π-accepting carbonyl ligands by a π-donor terminal oxo ligand on Mo(2) should increase this metal's affinity for other π-acid ligands. Both the semi-bridging carbonyl and the allylidene have π-acceptor capability and their closer interaction with Mo(2) in (IV) is consistent with the above reasoning. The closer Mo-Mo contact is probably a secondary effect of this tightening up of the bridging ligands to Mo(2).

The bond to the terminal oxo ligand, Mo(2)-O(3) is 1.705(2)Å. This is similar to Mo=O distances in other cyclopentadienylmolybdenum complexes, for example 1.688(9)Å in $[Mo_2(\mu\text{-}O)(SPh)_2(C_5H_5)_2(O)_2]$,[90] and 1.708(4)Å in $[Mo_3(O)(N)(CO)_4(C_5H_5)_3]$.[91]

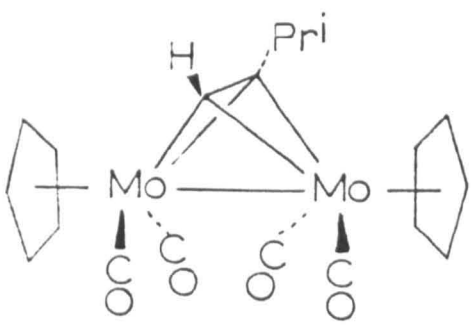
Structural Parameters for (IV) and (50)

Bond	IV	50
Mo-Mo′	2.881(1)	3.106(1)
Mo-C_α	2.088(3)	2.126(6)
Mo′-C_α	2.267(3)	2.249(5)
Mo′-C_β	2.284(3)	2.270(6)
Mo′-C_γ	2.492(3)	2.477(7)

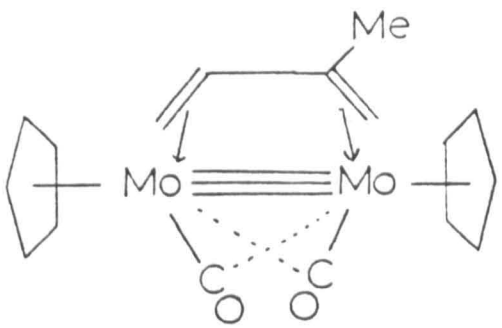
Thermolysis and Molecular Rearrangement of $[Mo_2(CO)_4(m\text{-}CHCHCMe_2)(C_5H_5)_2]$

Thermolysis of (50) in refluxing 1:1 toluene/hexane (3 h) yielded three main products which were separated by column chromatogaphy. The major product (40% yield) proved to be $[Mo_2(CO)_4(\mu\text{-}HCC^iPr)(C_5H_5)_2]$, (63), a member of a previously observed class of bridging alkyne complexes. These are more conveniently prepared by treatment of $[Mo(CO)_2(C_5H_5)]_2$ with the appropriate acetylene.[92,93]

The second product, (64), (20% yield), was identified by its spectroscopic data as an isoprene analogue of complex (I); $[Mo_2(CO)_2(\mu\text{-}\eta^4\text{-}CH_2CHCMeCH_2)(C_5H_5)_2]$.



(63)

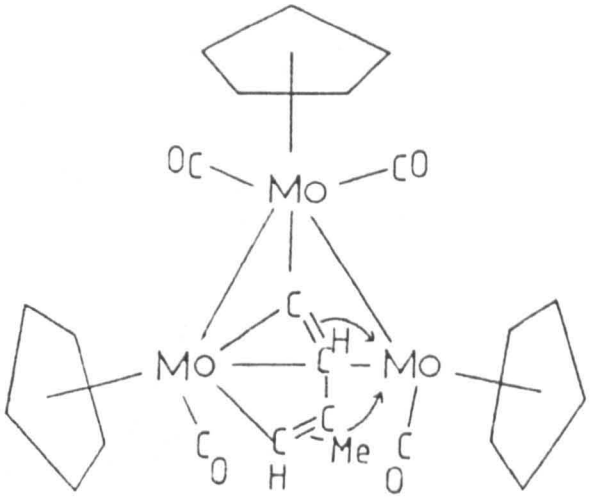


(64)

Unfortunately crystals of this material were not available for the structure determination necessary to compare the metal-diene bonding in the two compounds.

A third complex, (V), obtained in 10% yield could not be conclusively identified by spectroscopy alone. The presence of three cyclopentadienyl resonances in the ^1H and ^{13}C n.m.r. spectra were indicative of a trinuclear complex.

Its structure was thus determined by a single crystal x-ray diffraction study. The nuclearity of the complex was indeed three, which necessitated the solution of a 21 (Mo-Mo) vector Patterson map. This proved to be straightforward and the structure was subsequently refined to R = 0.026. The molecular structure of (V) is shown in Figure 2.16.



(V)

Compound (V) consists of an essentially equilateral triangle of molybdenum atoms, all at distances consistent with single bond formulation. The Mo-Mo bonds vary from 2.929(1)Å to 3.079(1)Å. Each metal possesses a cyclopentadienyl ligand. There are four carbonyl groups and an organic fragment which interacts with all three metals. This is derived from a single allylidene moiety of (50) by loss of three hydrogen atoms, one from the former carbene carbon and two from one of the methyl groups. The resulting four carbon chain is bound at both ends to Mo(1), forming part of a 2-molybda-4-methyl-molybdacyclopentadienyl unit (or molybdole), which is η-bound to Mo(2) and metallated by Mo(3) at the carbon C(5), α- to Mo(1).

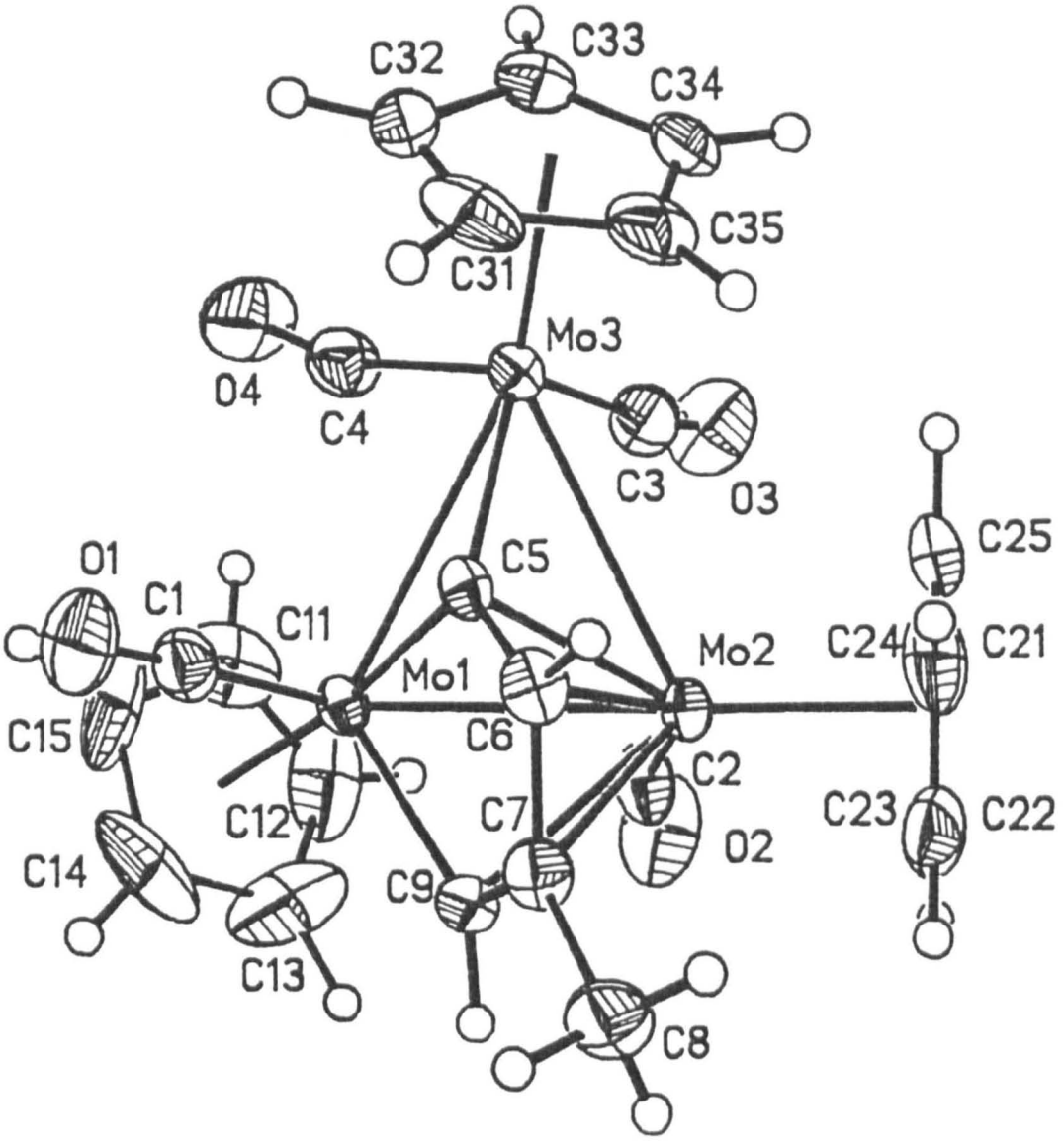

C32
C33
C34
C35
C31
Mo3
O4
C4
C3
O3
C25
O1
C1
C11
C5
C24
C21
Mo1
Mo2
C15
C6
C2
C12
C7
C23
C22
O2
C14
C9
C13
C8

Figure 2.16

Thus C(5) asymmetrically bridges the Mo_3 triangle (Mo(1)-C(5) = 2.709(5)Å, Mo(2)-C(5) = 2.200(5)Å and Mo(3)-C(5) = 2.048(4)Å) in a similar fashion to the μ_3- carbon atoms in $[H_2Os_3(CO)_9(CCH_2)]$,[94] and $[H_2Os_3(CO)_9(CCO)]$.[95] Reasonable electron counts are obtained at all three molybdenum atoms by consideration of the delocalised nature of the molybdole ring (see Figure 2.17). Thus Mo(1)-C(5) and Mo(1)-C(9) are not pure σ-bonds, but have additional π character as evidenced by their relatively short lengths, at 2.079(5)Å and 2.151(4)Å respectively. The corresponding bonds to Mo(2) are considerably longer at 2.200(5)Å and 2.361(4)Å.

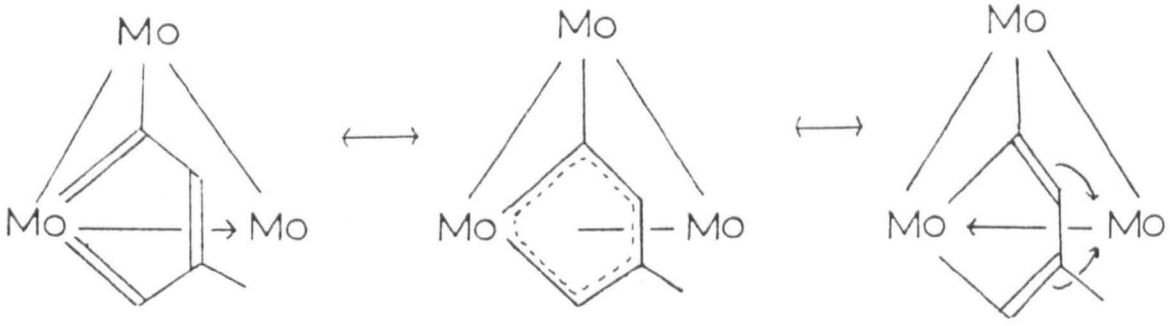


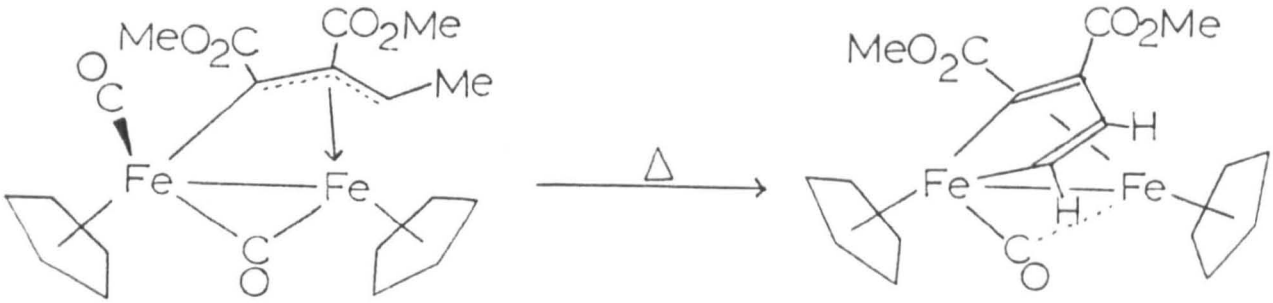
Figure 2.17

The molybdole functionality has been structurally characterised previously.[96]

Mechanism of Thermal Rearrangement of $[Mo_2(CO)_4(CHCHCMe_2)(C_5H_5)_2]$

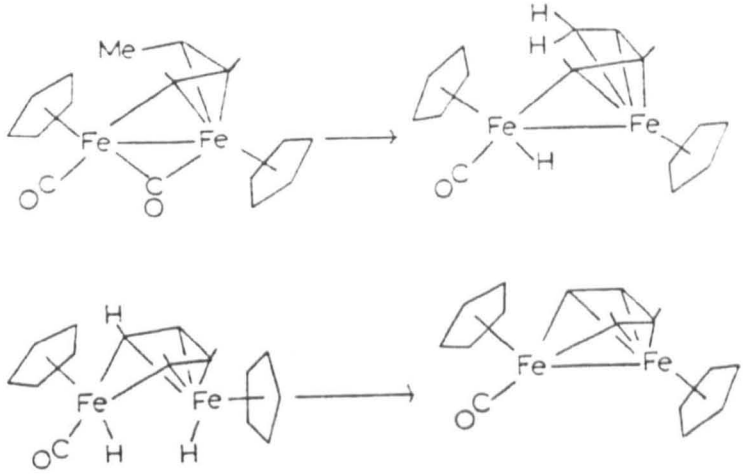
The formation of (V) implies that fragmentation of (50) is occuring under the reaction conditions. The exact nature of the fragments being unknown, the mechanism of its formation is obscure, and obviously complex.

It is noteworthy, however, that upon heating the μ-allylidene complex (65), $[Fe_2(CO)_2(CRCRCHMe)(C_5H_5)_2]$, R = CO_2Me, undergoes loss of two hydrogen atoms from a methyl group to yield the ferrole complex (66).[60]

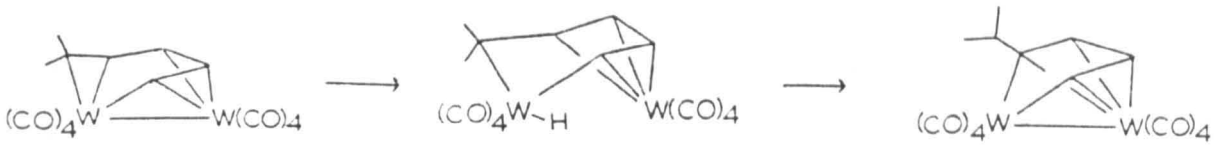


(65) (66)

Rudler et al. have attempted to explain this rearrangement by a mechanism involving metal-assisted hydrogen loss.[97]



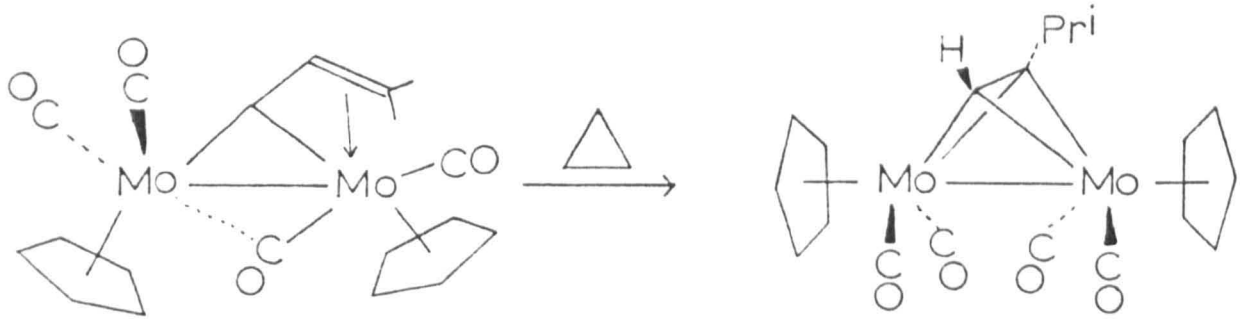
This proposal stemmed from their observation of a 1,2 hydrogen shift by which the ditungsten complex (56), $[W_2(CO)_8(\mu\text{-}\eta^3,\eta^3\text{-}CMeCMeCHCHCMe_2)]$ rearranges upon hexane reflux (1h) to the tungsten-tungstole complex (67).



(56) (67)

It is proposed that either an $^{\alpha}$- or $^{\beta}$- hydrogen abstraction occurs from C(2), with the result that W(2) possesses a hydride ligand. This may the be transferred to C(3), thus forming the isopropyl group by the reverse of a $^{\beta}$-elimination.

The thermal isomerisation of (50) to the μ-isopropylacetylene complex also involves a 1,2 hydrogen shift.

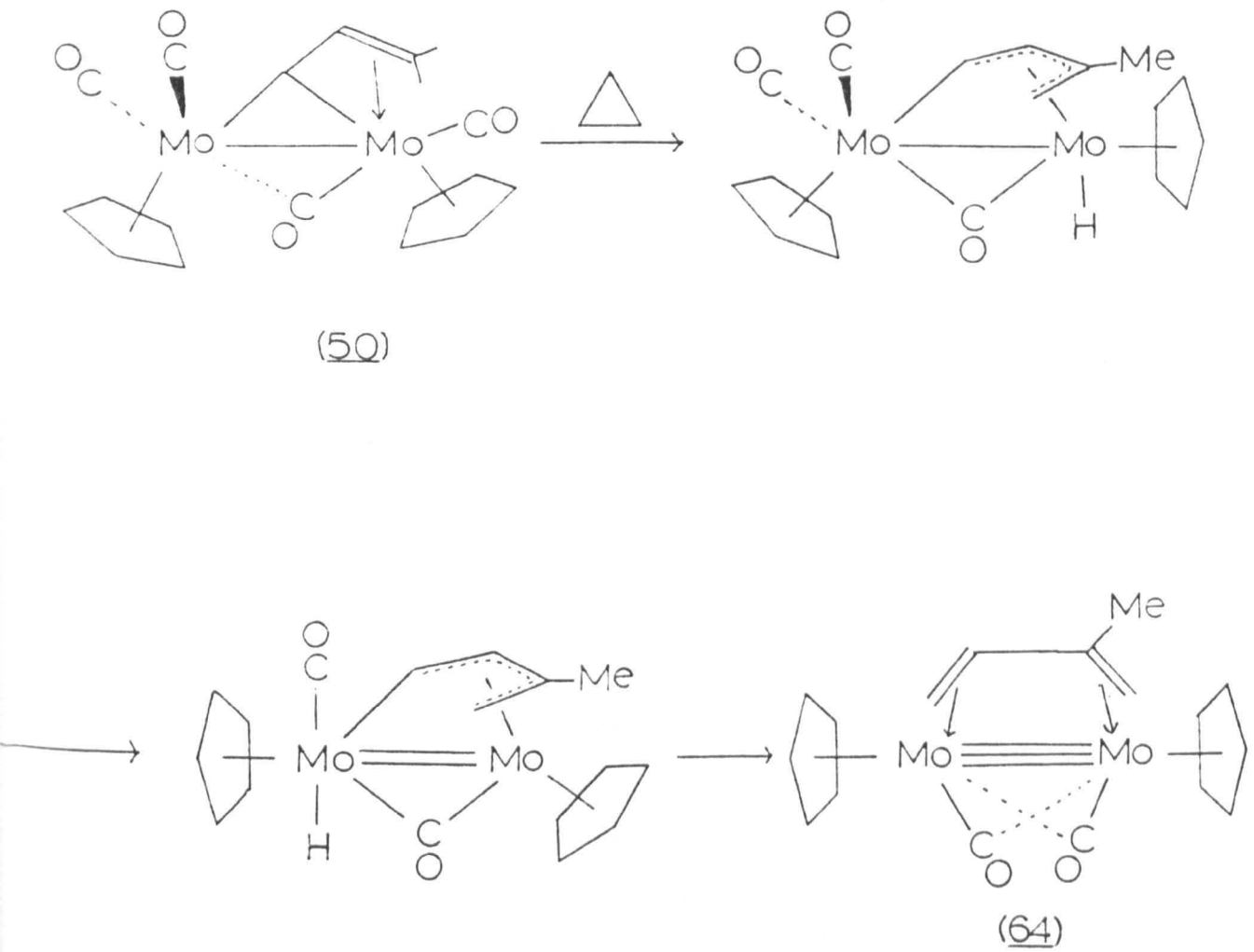


(50)

In order for $^{\beta}$-hydrogen abstraction to occur (from C(2) to Mo(2)), a rotation about the C(1)-C(2) bond must take place to bring the $^{\beta}$-hydrogen into contact with the metal. This may be accomplished after conversion of the μ-allylidene to a μ-η^1 vinylcarbene. The resulting μ-allenyl ligand would then insert into the metal-hydride to yield the observed complex (63), in which the acetylene lies transverse to the Mo-Mo axis.

A competing hydrogen abstraction process accounts for the formation of the μ-isoprene complex (64). This bears close resemblance to that occuring in the conversion of (65) to (66). A plausible mechanism is outlined in Scheme 2.10 below.

Scheme 2.10

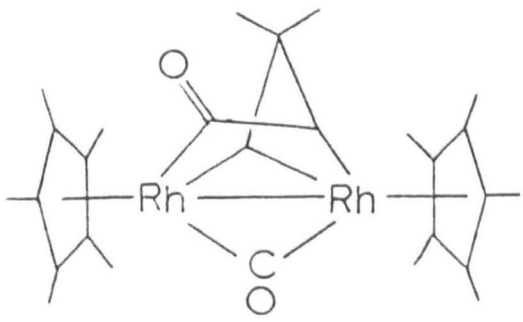


(50)

(64)

Reaction of 3,3-dimethylcyclopropene with $[Rh(CO)(C_5Me_5)]_2$

In order to further explore the reaction of cyclopropenes with unsaturated transition-metal systems, solutions of the rhodium 'double-bond' dimer $[Rh(\mu\text{-}CO)(\eta\text{-}C_5Me_5)]_2$, (18), were treated with a slight excess of 1 eq. of 3,3-dimethylcyclopropene. Reaction rapidly occured at 0^oc in either methylene chloride or hexane to yield a dark red crystalline complex (VI). Its i.r. spectrum displayed two absorptions in the carbonyl stretching region at 1809 and 1683 cm^{-1}. The n.m.r. spectra indicated that (VI) was a 1:1 adduct of the reactants.



(VI)

The amount of structural information available from these was greatly enhanced due to the spin activity of the ^{103}Rh nucleus. The (C_5Me_5) rings in (VI) appeared inequivalent as were the methyl groups derived from the cyclopropene, thus it seemed that molecular symmetry no longer related the two metal centres. One of the bridging carbonyl groups appeared to be intact, however the other was thought to have been involved in an insertion of some sort. Its ^{13}C resonance was a doublet (216 ppm, J = 23 Hz) thus showing coupling to just one of the metals.

From the former cyclopropene, there appeared to be a bridging C(H) carbon (178.5 ppm, dd, $^{1}J_{Rh-C}$ = 31.7, 19.5 Hz) and the other C(H) directly bonded to just one rhodium (53.6 ppm, d, J = 17.1 Hz).

This evidence was consistent with the molecular structure of (VI) shown above. However there existed a slight ambiguity in that a $^{1}H-^{1}H$ coupling of 2.8 Hz was observed between the two C(H) groups originating in the cyclopropene, suggesting that the 1,2 carbon-carbon bond of that moiety might still be intact. To clarify this problem an x-ray structure determination was undertaken on (VI). This clearly showed (Figure 2.18) that the cyclopropene 1,2 bond had been cleaved (C(3)...C(7) = 2.217(12)Å).

In the solid state (VI) consists of two Rh(η-C_5Me_5) units linked by a formal metal-metal bond (Rh(1)-Rh(2) = 2.624(2)Å), this has a length typical of bridged dirhodium structures, (Table 2.3)[98]

Table 2.3 Bridged Dirhodium Structures

Compound	Rh-Rh, Å	Ref.
$[Rh(\mu\text{-}CO)(\mu\text{-}COCHCMe_2CH)(\eta\text{-}C_5Me_5)_2]$, (VI)	2.624(2)	This work
$[Rh_2(phen)_2(O_2CH)_2Cl_2]$	2.576(4)	98
$[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$	2.665(1)	100a
$[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2]$	2.672(1)	100b
$[Rh_2(CO)_2\{\mu\text{-}C(CO_2Me)_2\}(\eta\text{-}C_5Me_5)_2]$	2.663(1)	100c
$[Rh_2(\mu\text{-}CO)_2(\mu\text{-}C_5Br_4)(\eta\text{-}C_5Me_5)_2]$	2.612(3)	100c
$[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_2]$	2.743(1)	99

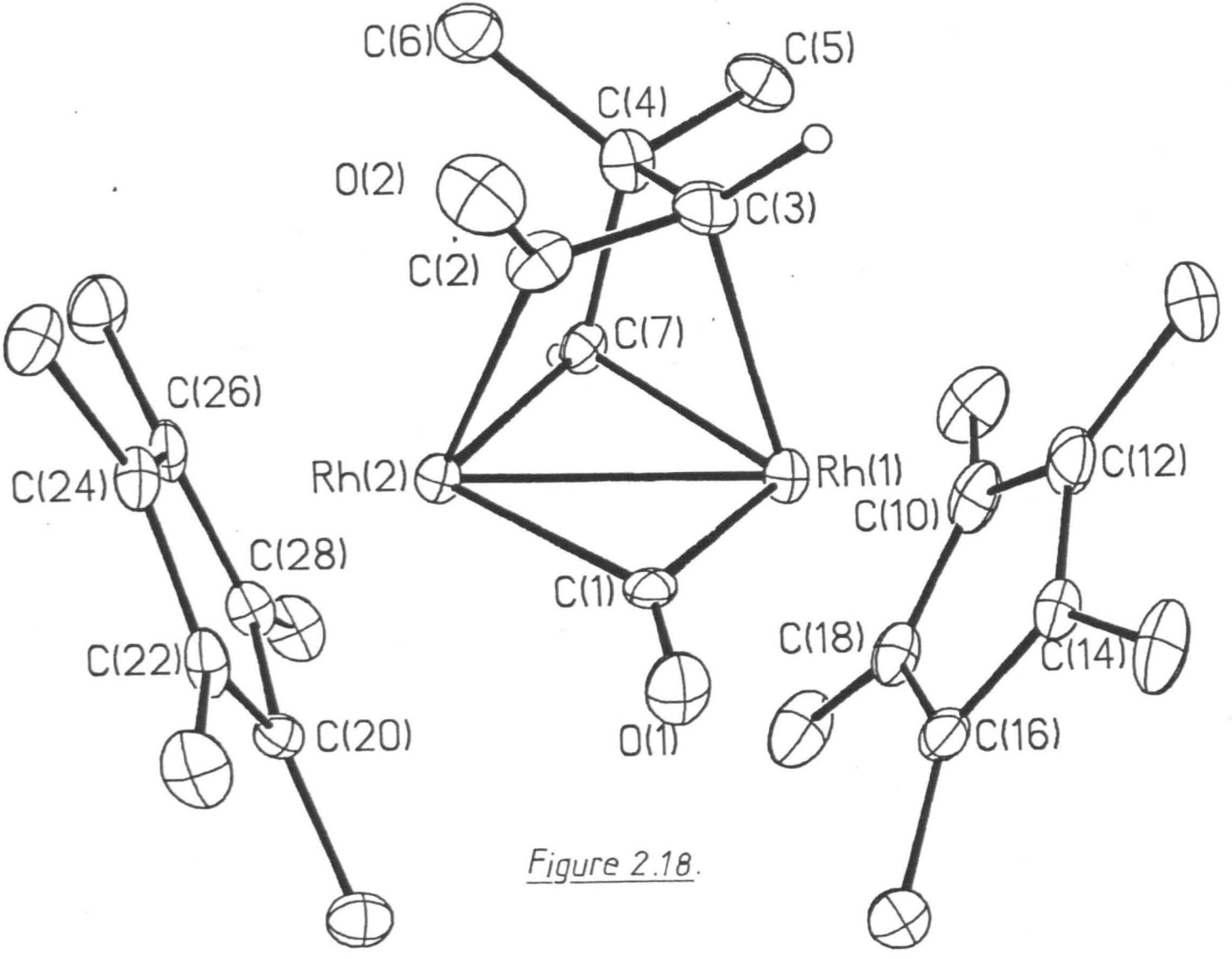

C(6)
C(5)
C(4)
O(2)
C(3)
C(2)
C(7)
C(26)
C(24)
Rh(2)
Rh(1)
C(12)
C(10)
C(28)
C(1)
C(18)
C(14)
C(22)
C(20)
O(1)
C(16)

Figure 2.18.

In (VI) the rhodiums are symmetrically bridged by a carbonyl ligand [Rh(1)-C(1) = 1.988(8)Å, Rh(2)-C(1) = 2.010(7)Å], which is similar to the μ-CO in $[Rh_2(CO)_3(\eta\text{-}C_5Me_5)]$, for which Rh-C = 1.962(8), 1.975(11)Å.[99] Also bridging is a ligand derived from the other carbonyl of the dirhodium starting material and the 3,3-dimethylcyclopropene; $\mu\text{-}(\eta^2,\eta^2\text{-}COCHCMe_2CH)$. This binds to the Rh_2 fragment via a μ-carbene functionality [C(7)] and a μ-ketene group [C(2),C(3)]. The μ-carbene carbon is symmetrically disposed between the two metals; Rh(1)-C(7) = 2.059(8)Å, Rh(2)-C(7) = 2.050(8)Å, these distances being typical of other dirhodium μ-carbene complexes (see Table 2.4)[100]

Table 2.4. Dirhodium μ-Carbene Structures

Compound	Rh-C, Å	Ref.
$[Rh(\mu\text{-}CO)(\mu\text{-}COCHCMe_2CH)(\eta\text{-}C_5Me_5)_2]$ (VI)	2.059(8) 2.050(8)	This work
$[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$	2.029(4) 2.055(4)	100a
$[Rh_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2]$	2.026(8)	100b
$[Rh_2(CO)_2\{\mu\text{-}C(CO_2Me)_2\}(\eta\text{-}C_5Me_5)_2]$	2.078(7) 2.072(6)	100c
$[Rh_2(\mu\text{-}CO)_2(\mu\text{-}C_5Br_4)(\eta\text{-}C_5Me_5)_2]$	2.103(15) 2.118(11)	100c

As a result of the carbonyl insertion the other (proposed) carbene moiety has become singly bound to just one of the metal centres; Rh(1)-C(3) = 2.191(9)Å. This bond is very long for a rhodium-carbon σ-bond. For example, Rh-C = 2.081(9)Å in $[Rh(PPh_3)(CH_3)I_2]$[101] and 2.08(3)Å in $[Rh(CO)(C_2F_5)(C_5H_5)I]$.[102] Thus it would appear that Rh(1)-C(3) is a weak bond, its elongation probably due to relief of ring strain.

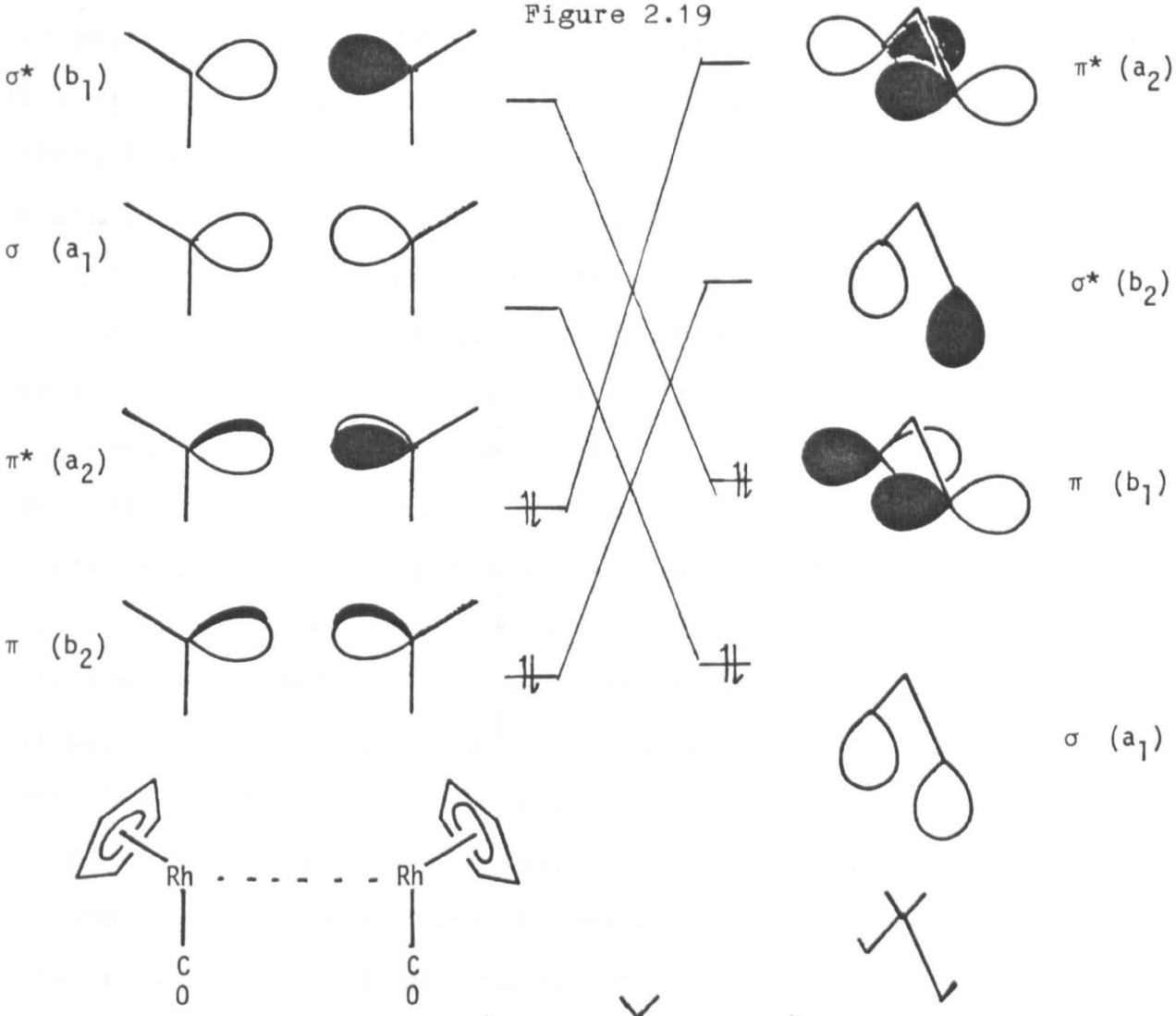
The Rh(2)-C(2) bond is 2.065(8)Å, which is quite typical for a rhodium-acyl bond. Two other molecules possessing this structural unit have been crystallographically determined. The compound $[Rh(CO)(COCH_3(\mu\text{-}I)I_2]_2^{2-}$ has a Rh-C(acyl) bond of 2.06(2)Å,[103] whereas the corresponding linkage in $[Rh(PPh_3)(COEt)(S_2C_2(CN)_2)I]$ is 2.01(1)Å long.[104]

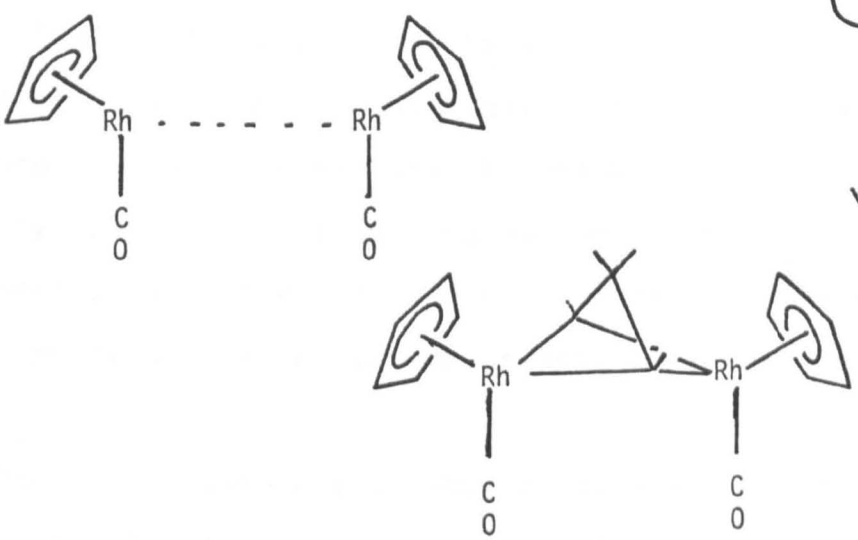
The carbon-carbon bonds of the bridging ligand are those expected for a saturated system; the shortest is C(2)-C(3) at 1.485(12)Å and the longest C(3)-C(4) which is 1.566(10)Å. The acyl C(2)-O(2) bond of 1.215(10)Å is of comparable length to the ketone function found in (I) at 1.207(4)Å, the conclusion being that π-backbonding to the CO π^* orbital is not significant in (VI).

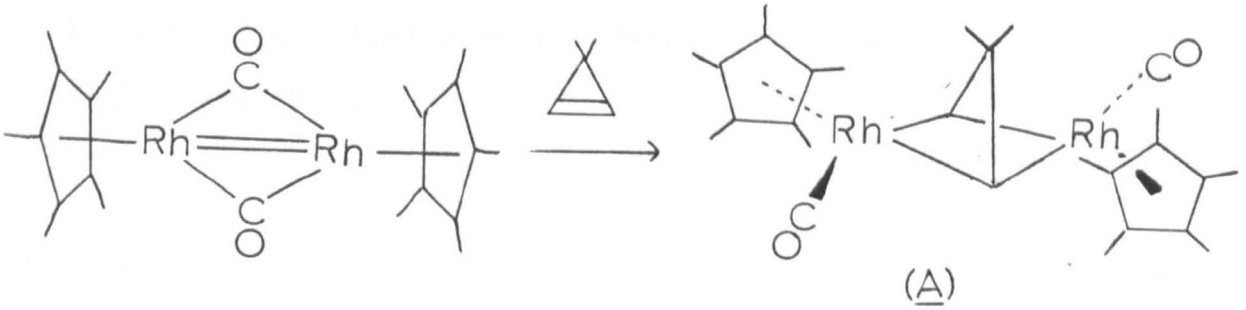
Mechanism of the Formation of (VI)

Formation of (VI) is thought to occur via a doubly bridged carbene intermediate (A). Although there is no evidence for direct observation of this species, it is proposed as the most likely kinetic product of the reaction between cyclopropene and the rhodium dimer on the basis of their frontier orbitals. (Figure 2.19).

Figure 2.19


σ* (b1)
σ (a1)
π* (a2)
π (b2)
π* (a2)
σ* (b2)
π (b1)
σ (a1)


Rh
Rh
C
O
C
O
Rh
Rh
C
O
C
O


O
C
Rh
Rh
C
O
Rh
Rh
C
O
C
O

(A)

The frontier orbitals of the unbridged rhodium dimer heve already been introduced (see Section 2.1). Those of the doubly bridged dimer have also been calculated.[105] This allows visualisation of the initial interaction of the cyclopropene with [Rh(μ-CO)(η-C_5Me_5)]. (The substitution of (C_5Me_5) for (C_5H_5) should not make a great difference to the qualitative arguments given here).

The frontier orbitals of (18) are shown in Fig. 2.19. The LUMO ($2b_2$) may act as a π-acceptor orbital, so that if the cyclopropene approaches in a transverse sense (i.e. with the C=C vector orthogonal to the Rh-Rh one), $2b_2$ should mix with the cyclopropene π-orbital. The HOMO a_2 orbital would have δ-symmetry with respect to the incoming cyclopropene and is set up to interact with the π^*-orbital of the organic moiety. The next lowest orbital, a_1, may mix with the σ-orbital of the cyclopropene and below that $1b_2$ will be expected to interact with the cyclopropene ! level (having the same symmetry as the $2b_2$ LUMO).

A picture of the redistribution of electrons when the two fragments are brought together may thus be obtained from the considerations above. Firstly the π- bond of the cyclopropene would be lost- the π^*-orbital has been populated by its in-phase combination with the a_2 orbital of the dirhodium fragment and the π-orbital itself depopulated by donation to $2b_2$.

The sigma component of the cyclopropene double bond may also have been lost. The filled a_1 orbital would mix with the filled cyclopropene σ-orbital to produce a low-energy bonding combination which would also be filled and a higher energy out-of-phase combination, which may be thought of as 'Rh-C σ^*'.

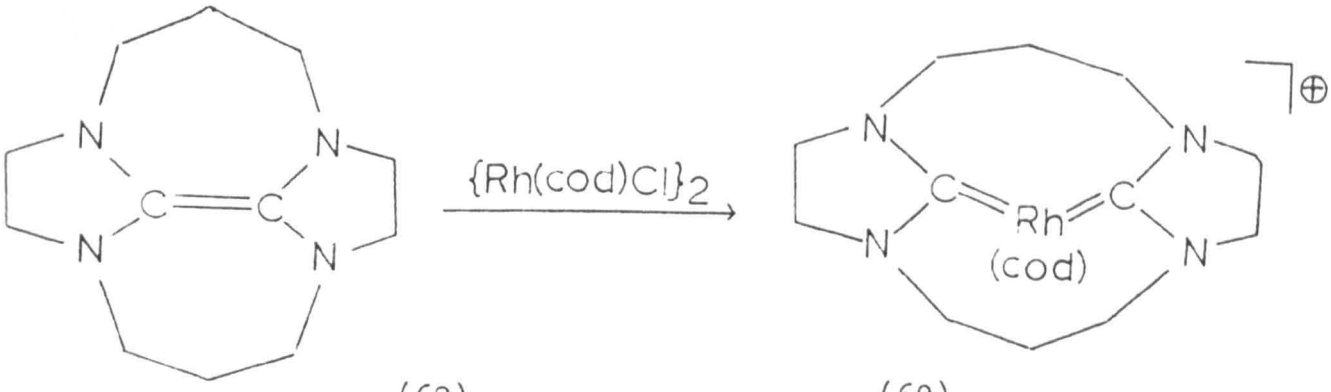
This latter will only be filled, however, if it is of lower energy than the cyclopropene σ^*-orbital- otherwise this will become populated and the C=C sigma bond will have been lost also.

The above analysis, though, does not take into account geometric changes which would be expected to occur as the two molecular fragments react. A probable consequence would be the transformation of the bridging carbonyl groups to terminal geometries. Otherwise the rhodium atoms would be quadruply bridged, a geometric arrangement which has yet to be encountered. If this is so, the alternative analysis of the interaction of the cyclopropene with the unbridged dicarbonyl dimer may also be of relevance. In this case the frontier orbitals of $[Rh(CO)(C_5H_5)]_2$ would be those used by P. Hofmann.

If this investigation is carried out it is apparent that once again there are orbitals of the correct symmetry and energy to interact with the cyclopropene π-, π^*- and σ- orbitals. In addition though, the LUMO of the Rh_2 species (π^*_{xy} in Hofmann's nomenclature) is set up to mix with the cyclopropene σ^*-orbital. Thus it is reasonable to assume that the cyclopropene double bond is cleaved in a concerted manner and the dicarbene (A) formed upon initial reaction. All that is then required to yield (VI) is a carbonyl insertion into one of the four Rh-C(carbene) σ-bonds and the migration of the other carbonyl back to a bridging position to maintain an electronic balance at the two metals.

Fragmentation of the C=C double bond of a cyclopropene represents a previously unobserved mode of reactivity for these molecules at transition-metal centres. It is of particular interest when viewed as the reverse of carbene coupling reactions, the importance of which may lie in olefin formation during the Fischer-Tropsch process.[59]

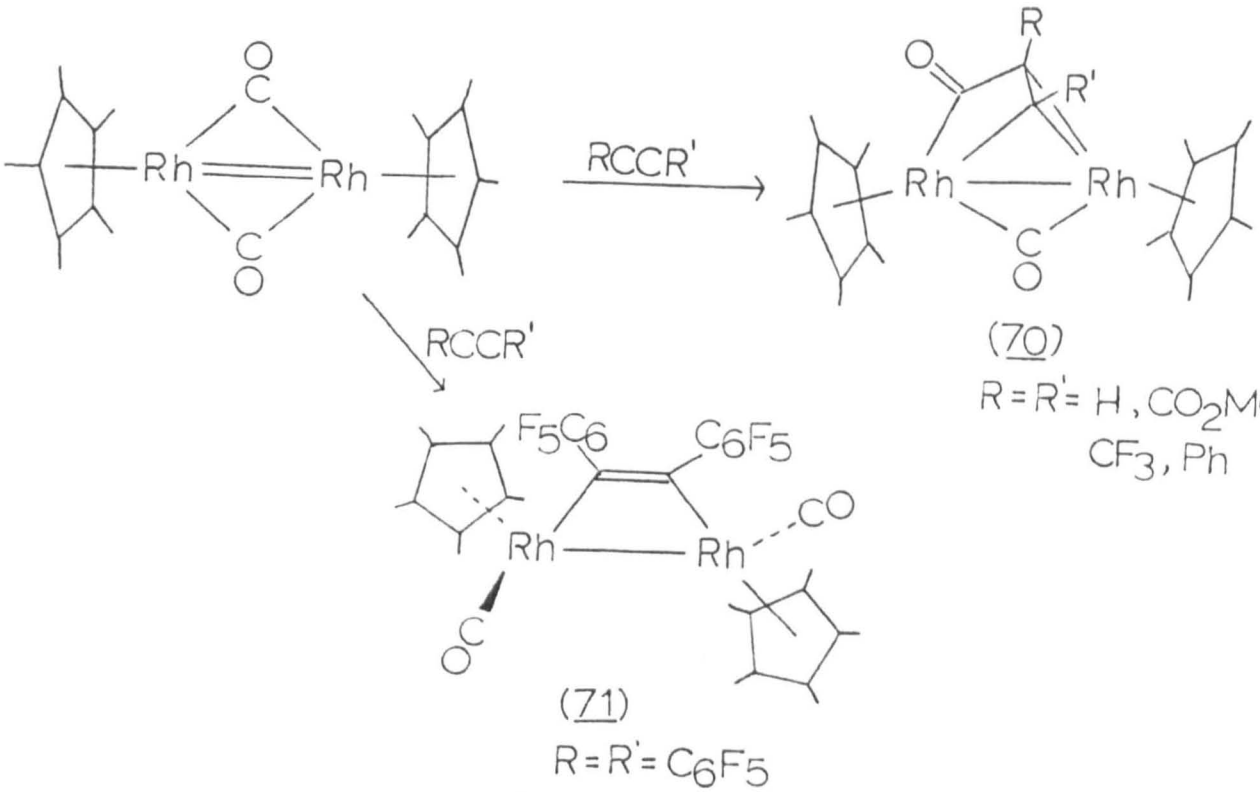
Examples of this coupling process have been observed in molecular systems; olefin formation occuring in the thermal decomposition of di- and tri-metal μ-dicarbene species.[106,107] Conversely fragmentation of an electron rich olefin (68), to yield a dicarbene complex (69) has been reported for a mononuclear rhodium system by Lappert et al.[108]



(68) (69)

A discussion of carbene coupling/ alkene fragmentation at single metal centres from a theoretical standpoint has also appeared.[109]

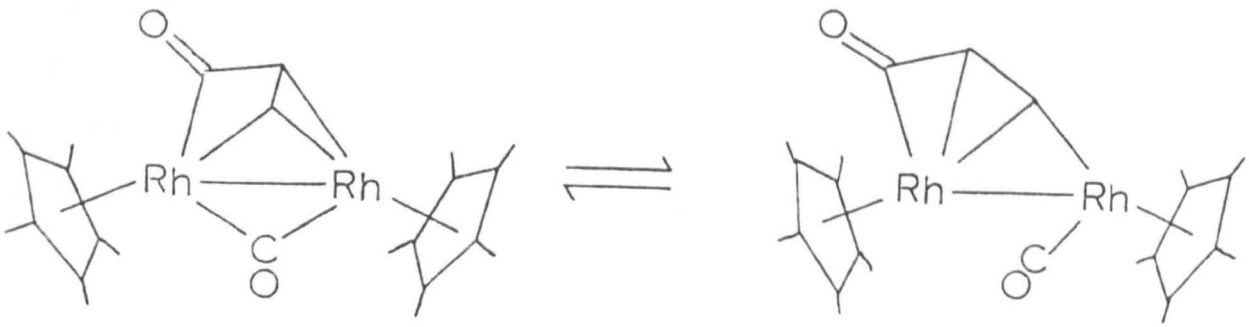
It should be noted, however, that in their reactivity, cyclopropenes are often seen to parallel that of alkynes more closely than that of olefins. The reaction of $[Rh(\mu\text{-}CO)(C_5Me_5)]_2$ with various acetylenes has been studied.[110,111] The results (summarised in Scheme 2.11) bear a close resemblance to that observed for 3,3-dimethylcyclopropene. The only alkyne which did not yield a structural analogue, (70), to (VI) was $C_2(C_6F_5)_2$ which gave instead an addition product (71) in 75% yield in which the alkyne bridges the rhodiums in a $\mu\text{-}\eta^1,\eta^1$ fashion. Interestingly this could not be induced to undergo transformation to the isomer $[Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}COC_2(C_6F_5)_2)(C_5Me_5)_2]$, a result which does not provide evidence for the intermediacy of ($\mu\text{-}\eta^1,\eta^1$-alkyne) complexes in the formation of the compounds (70).



Scheme 2.11

The compounds (70) were characterised spectroscopically and the hexafluorobut-2-yne derivative was structurally analysed. The x-ray results of the compound show similar features to (VI). The Rh-Rh bond is slightly longer at 2.687(1)Å; the carbene carbon is at 2.009(8)Å and 2.057(8)Å from the metals. Once more the rhodium-acyl bond is short for a Rh-C linkage- 2.049(10)Å, and the remaining carbon of the μ-C_3 unit is found to be 2.167(9)Å from the nearest rhodium. This corresponds to the long Rh(1)-C(3) bond in (VI).

For the C_2H_2 derivative, (70a), Herrmann et al. have observed the interconversion of the (μ-η^2,η^2-COCHCH) ligand to a (μ-η^1,η^3) form, in which the bridging carbonyl moves to a terminal site.

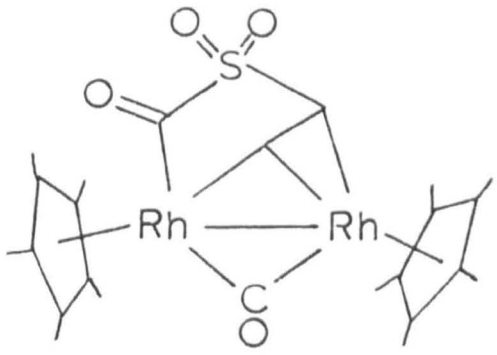


(70a)

A similar intramolecular process has been proposed by Knox et al.[112] for the interconversion of the metallacycles
$[M_2(\mu\text{-CO})(CO)(\mu\text{-}\eta^1,\eta^3\text{-CHCHCO})(C_5H_5)_2]$, M = Fe,Ru to
$[M_2(\mu\text{-CO})_2(\mu\text{-}\eta^2,\eta^2\text{-COCHCH})(C_5H_5)_2]$.

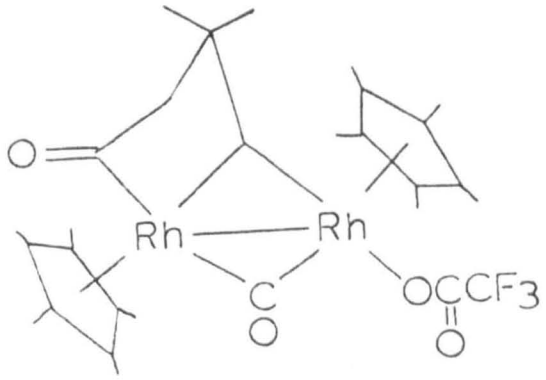
Evidence for fluxionality in (VI) has not been observed. Its conversion to a η^1,η^3 isomer would require cleavage of the long Rh(1)-C(3) bond and its replacement by a Rh(2)-C(3) interaction. In (VI) the Rh(2)..C(3) internuclear separation is only 2.823Å so that this kind of isomerisation might not be too unlikely.

The reactivity of (VI) and its acetylene congeners has so far been little explored; (70a) has been observed to incorporate sulphur dioxide at -40°c to give (72).[111]



(72)

Protonation of (VI) with trifluoroacetic acid was regiospecific giving (73) in high yield.[73] Thus the abnormally long Rh-C bond of (VI) has been cleaved. This was in contrast to the expected result of attack at the μ-carbene carbon atom.

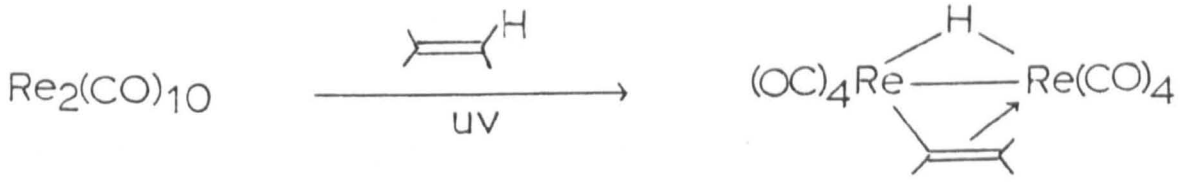


(73)

Analogues of (VI) have been prepared using other metal dimers of the form $[MM'(\mu\text{-}CO)_2(C_5Me_5)_2]$, where M = M' = Co ; M = Co, M' = Rh,Ir and M = Rh, M' = Ir.[113] These show a similar reactivity to (VI) with respect to CF_3COOH.[73]

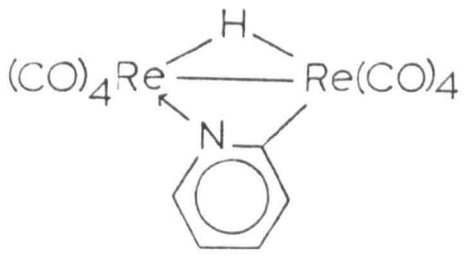
Reaction of 3,3-dimethylcyclopropene with $[Re_2(\mu\text{-}H)(\mu\text{-vinyl})(CO)_8]$

Photolysis of hexane or toluene solutions of $[Re_2(CO)_{10}]$ in the presence of 1-alkenes had been recently reported by Brown and coworkers to yield the μ-hydrido, μ-alkenyl complexes (74).[114]



(74)

Thermolysis of 1,2-dieq.$[Re_2(CO)_8(py)_2]$ had been observed previously to give (75),[115] presumably by dissociative loss of pyridine and subsequent oxidative addition of a pyridine C-H bond.



(75)

Further, when $[Re_2(CO)_{10}]$ is photolysed in the presence of P- donor ligands, (L), disubstituted binuclear compounds 1,2-$[Re_2(CO)_8L_2]$ result,[116] the mechanism of their formation being as follows.

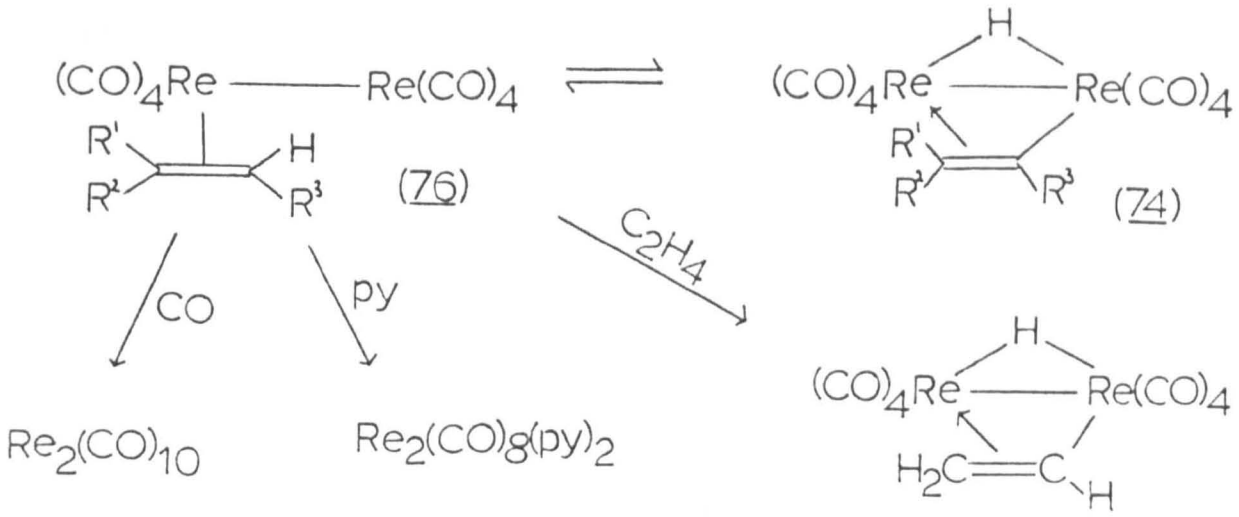
$$Re_2(CO)_{10} \xrightarrow{h\nu} 2\ Re(CO)_5^{\bullet}$$

$$Re(CO)_5^{\bullet} \xrightarrow{L} Re(CO)_4L^{\bullet} + CO$$

$$2\ Re(CO)_4L^{\bullet} \longrightarrow 1,2\text{-}Re_2(CO)_8L_2$$

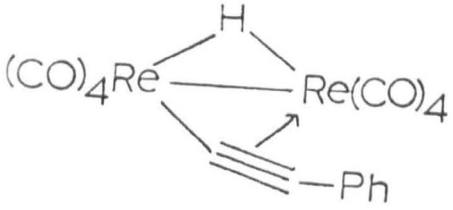
It is therefore likely that formation of (74) proceeds via a 1,2-$[Re_2(CO)_8(alkene)_2]$ intermediate, which upon loss of an olefin ligand undergoes a similar intramolecular oxidative addition to that observed for the (bis)pyridine complex.

However whereas the μ-pyridyl function in (75) is quite stable, the -vinyl complexes possess a reactivity which indicates the reversibility of the oxidative process. Addition, under mild conditions, of CO (rt, 1 atm.) to (74) regenerates $[Re_2(CO)_{10}]$ and treatment of (74) with several nucleophiles (L') e.g. pyridine, yields 1,2-$[Re_2(CO)_8L'_2]$ with evolution of the 1-alkene. Both of these reactions may be explained by the intermediacy of (76)-$[Re_2(CO)_8(alkene)]$.

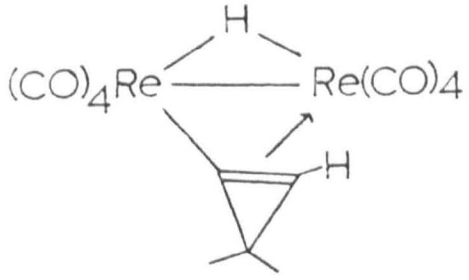


Similarly, the reversible isomerisation of (70)-(72) accounts for the facile exchange of the alkenyl ligand; for example all the substituted μ-vinyl complexes react with ethylene to give $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CHCH_2)]$, (74a).

Phenylacetylene had also been observed to react with one of the substituted μ-vinyl compounds, (74b), ($R_1 = R_3 = H$, $R_2 = Et$), the major product being (77).[114]



(77)



(78)

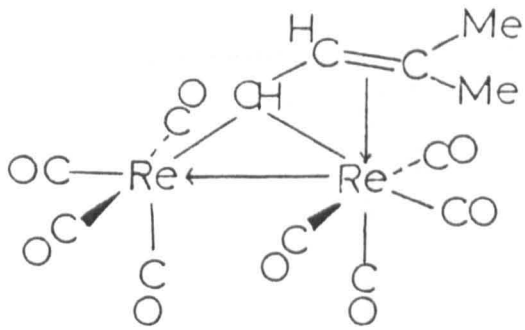
It was therefore expected that 3,3-dimethylcyclopropene should react with (74) whether regarded as a simple olefin or as a homo-acetylene. Formation of a μ-cyclopropenyl ligand had not previously been reported, however, so that it was of interest to see if oxidative addition of the cyclopropene C-H bond would occur to give (78).

Accordingly an excess of 3,3-dimethylcyclopropene was added to a hexane solution of the 1-butenyl complex (74b) and stirred in a sealed tube for 3 days at room temperature.

One product, (VII), was obtained upon column chromatography of the reaction mixture. On the basis of spectroscopic evidence it was found to have an empirical formula $[Re_2(CO)_8(\text{cyclopropene})]$. The structure (78) was ruled out by the absence of a high-field hydridic proton resonance in the ^1H n.m.r. spectrum.

The characteristic ^{13}C and ^1H n.m.r. shifts that had been observed for the bridging allylidene ligand (μ-η^1,η^3-$CHCHCMe_2$) in Mo_2 and W_2 complexes were also apparent for (VII) although there was an unusually high ^1H-^1H coupling constant.

Eight terminal carbonyl resonances were found in the ^{13}C spectrum of (VII). In the absence of other bridging ligands the formulation of (VII) as a (μ-η^1,η3-allylidene) complex seemed worrying on electron counting grounds and the possibility that (VII) was a μ-η^1-vinylcarbene species with a formal Re=Re double bond remained.



(VII)

A crystal structure analysis revealed though that (VII) was indeed $[Re_2(CO)_8(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCMe_2)]$. The molecular geometry of which is shown in Figure 2.20 with the atomic labelling scheme.

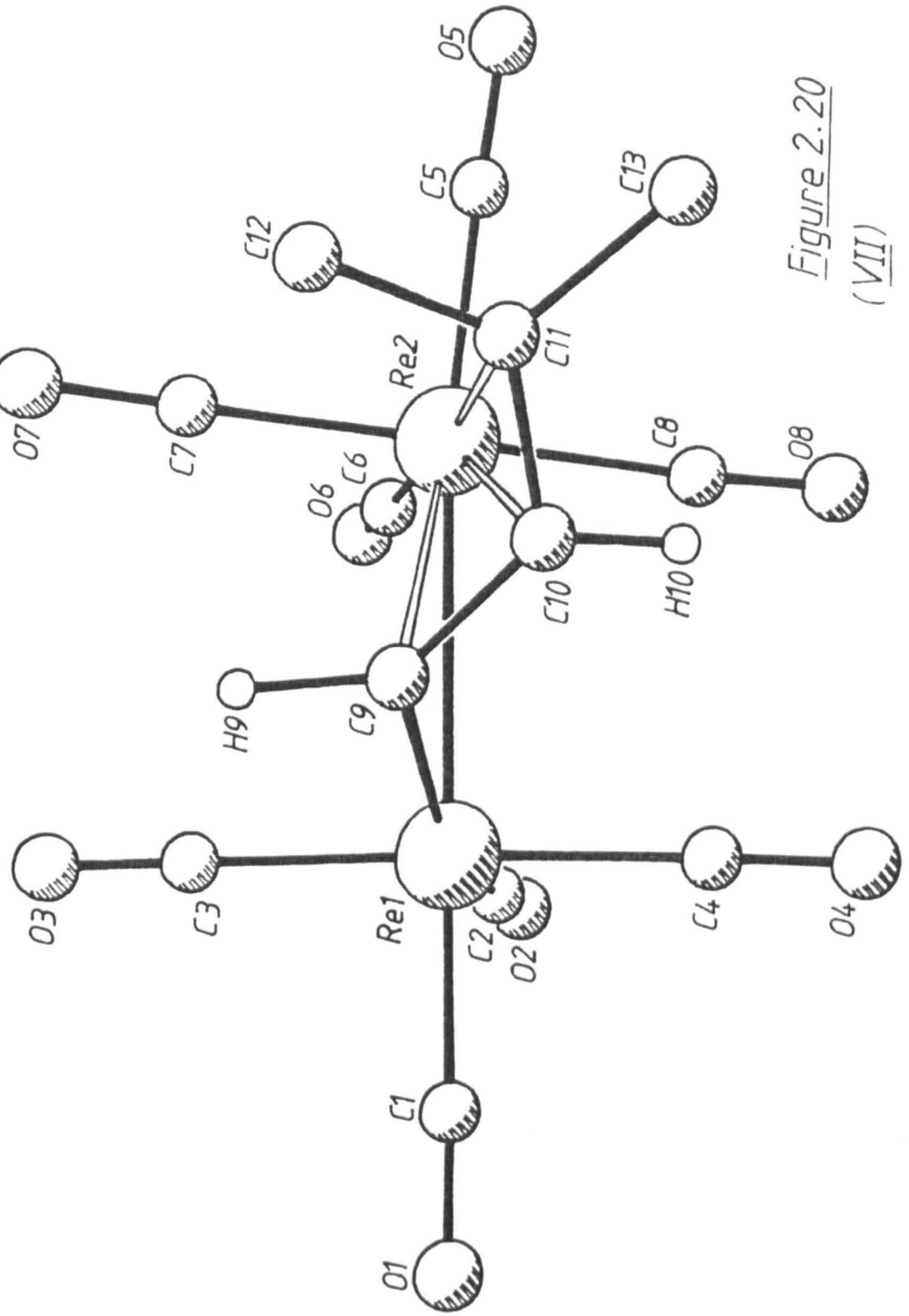


Figure 2.20
(VII)

In (VII) two $Re(CO)_4$ units are linked by a Re-Re bond of 3.058(1)Å and are bridged by the μ-allylidene ligand. The metal-metal bond falls in the range observed for Re-Re single bonds as shown in Table 2.5.[117]

Table 2.5. Rhenium-Rhenium Single Bonds

Compound	Re-Re, Å	Ref.
$[Re_2(\mu\text{-}CO)(CO)_4(\eta\text{-}C_5H_5)_2]$	2.957(1)	117a
$[Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-}H)(\mu\text{-}NCHMe)]$	3.035(3)	117b
$[Re_2(CO)_{10}]$	3.041(1)	120
$[Re_2(CO)_8(\mu\text{-}CHCHCMe_2)]$ (VII)	3.058(1)	This work
$[Re_2(CO)_8(\mu\text{-}SiPh_2)(H)_2]$	3.121(2)	117c
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\{\eta^2\text{-}NC_5H_4\})]$	3.202(1) av.	115b
$[Re_2(CO)_7(\mu\text{-}H)(\mu\text{-}\{\eta^2\text{-}NC_5H_4\})(ONMe_3)]$	3.232(1)	115b

The main feature of structural interest in (VII) is the $(\mu\text{-}CHCHCMe_2)$ ligand. This is η^1 bound to Re(1)- [Re(1)-C(9) = 2.109(11)Å] and η^3 bound to Re(2)- [Re(2)-C(9) = 2.353(11)Å, Re(2)-C(10) = 2.281(11)Å and Re(2)-C(11) = 2.494(13)Å]. These rhenium-carbon bond lengths are put in perspective by reference to Table 2.6.[118] The μ-carbene carbon C(9) bridge in a highly asymmetric fashion - the bond to Re(1) being similar in length to rhenium-formyl and methoxycarbene linkages and indicating a bond order between 1 and 2. The Re(2)-C(9) distance, on the other hand, is much longer and falls on the limit of normal Re-C σ-bond lengths.

Table 2.6. Rhenium-Carbon σ-Bonds

Compound	Re—C, Å	Ref.
$[Re_2(CO)_4(\mu\text{-}\{\eta^1,\eta^2C{=}CPhCPh{=}CH_2\})(\eta\text{-}C_5H_5)_2]$	1.90(2) (Re=C) 2.21, 2.31(2)	118a
$[Re(CO)_2(CHSiMe_3)(\eta\text{-}C_5H_5)]$	1.92(2)	118b
$[Re_2\{\mu\text{-}C(SiMe_3)_2\}(CH_2SiMe_3)_4]$	1.93(1) (Re-μ-C)	118c
$[Re(CO)_2\{C(Ph)PMe_3\}(\eta\text{-}C_5H_5)][BCl_4]$	1.97(1)	118d
$[Re(PPh_3)(NO)\{C(H)O\}(\eta\text{-}C_5H_5)]$	2.055(10)	118e
$[Re(CO)_4\{C(Me)OMe\}Mn(CO)_5]$	2.094(7)	118f
$[Re_2(CO)_8(\eta\text{-}CPh)(\mu\text{-}Br)]$	2.14(4)	118g
$[Re_2Me_8][Li]_2$	2.19(1)	118h
$[Re(CO)(PMe_3)_2(NO)(CH_3)(\eta^1\text{-}C_5H_5)]$	2.26 C(methyl) 2.32 C(Cp)	118i
$[Re(CO)_2(CH_2Ph)(H)(\eta\text{-}C_5H_5)]$	2.29(1)	118j
$[Re(CO)_5(\mu\text{-}\{\eta^1,\eta^1,CH_2CH_2\})Re(CO)_5]$	2.30(1)	118k
$[Re(CO)_4(\eta^2\text{-}CH_2CH_2PPh_2]$	2.31(1)	118l

Carbon atom C(10) is more tightly bound to Re(2) and compares with the olefinic carbons in the cyclopentene complex (79), $[Re(PMe_2Ph)_3(\eta^2\text{-}C_5H_8)H_3]$ which are 2.267 and 2.275(14)Å from the metal.[119] The Re(2)-C(11) bond length is over 0.2Å longer than these and must represent only a weak interaction between thes two atoms. The C(10)-C(11) distance of 1.385(18)Å is shorter than other C_β-C_γ bonds in structurally characterised μ-allylidene complexes (Table 2.7) and supports the view that the C(10)-C(11) unit is not strongly π-bound to Re(2). It should be noted that the relatively high e.s.d. of this bond weakens this argument somewhat. The C(9)-C(10) bond is longer at 1.441(16)Å and typical for C_α-C_β.

The carbonyl ligands in (VII) are all linear, the Re-C-O angles ranging from 175(1) to 180(1)°, and terminal in character. The Re-C(O) bonds are between 1.89(1)Å and 2.00(1)Å. The longest are for the mutually trans carbonyls [C(3)-O(3) and C(4)-O(4)] and [C(7)-O(7) and C(8)-O(8)]. The shortest are the axial ligands [C(1)-O(1) and C(5)-O(5)]. These findings are in accord with the recently redetermined structure of $[Re_2(CO)_{10}]$,[120] in which the axial Re-C(O) was found to be 1.929(7)Å; 0.058Å shorter than the average equatorial Re-C(O) bond length of 1.987(15)Å. The accepted model for metal-carbonyl bonding explains these results in terms of competition for d_π-electron density between mutually trans pairs of carbonyl ligands.

The two $Re(CO)_4$ units are staggered with respect to each other by approximately 20°. (e.g. the torsion angle C(3)-Re(1)-Re(2)-C(7) = 18.6°). This lies between the staggering of 45° in dirheniumdecacarbonyl which possesses approximate D_{4d} symmetry and the nearly eclipsed geometry

Table 2.7. Geometry of μ-Allylidene Complexes

COMPLEX	M–M'	M–C_α	M'–C_α	M' C_β	M'–C_γ
$Cp_2Ru_2(CH_2)(CPhCPhCH_2)$	2·713(1)	2·081(7)	2·089(7)	2·152(7)	2·142(8)
$Cp_2Fe_2(CO)_2\{C(CO_2Me).C(CO_2Me)CHMe\}$	2·540(2)	1·968(12)	1·969(2)	2·04(1)	2·11(1)
$Cp_2Ru_2(CO)_2\{CMeCMeCH_2\}$	2·719(1)	2·083(3)	2·125(2)	2·168(2)	2·180(2)
$W_2(CO)_9\{CHCHCMe_2\}$	3·189(2)	2·20(2)	2·18(2)	2·31(2)	2·63(3)
$Os_4H_2(CO)_{11}\{CMeCPhCHPh\}$	2·798(2)	2·2 (2)	2·16(2)	2·26(2)	2·32(1)

found for $[Re_2(CO)_8(\mu\text{-}NC_5H_4)(\mu\text{-}H)]$ in which the C-Re-Re-C torsion angles are less than 6^o.

It is of interest to compare the geometry of the μ-allylidene ligand in (VII) with that of the isoelectronic ditungsten species $[W_2(CO)_9(\mu\text{-}CHCHCMe_2)]$, (53). Major differences would be expected because in (VII) the allylidene ligand bridges two ML_4 units and in (53) an ML_4 and a ML_5 fragment. Unfortunately the x-ray results for (53) do not appear reliable as the C_α-C_β distance of 1.24(3)Å is too short to be physically sensible and a structure redetermination would seem desirable. The parameters for the analogue $[W_2(CO)_9(\mu\text{-}CMeCMeCH(CHCMe_2))]$ (55), may be contrasted with those of (VII) with more confidence. The crucial change is in the position of the bridging carbon. In (53) this is closer to the $W(CO)_4$ centre (2.18(3)Å) than the $W(CO)_5$ centre (2.22(3)Å). This is even more marked in the triosmium complex (46c) $[H_2Os_3(CO)_{11}(\mu\text{-}\eta^1,\eta^3\text{-}CMeCPhCHPh)]$. Again the metal [Os(1)] to which the allylidene is η^1-bound possesses one more CO ligand than the metal [Os(2)], which is η^3 coordinated. The μ-carbene carbon is 2.24(2)Å from Os(1) yet only 2.16(2)Å from Os(2).

Clearly μ-allylidene ligands can show considerable flexibility in their bonding to transition metals, reflecting the electronic requirements of those metal centres.

This has already been discussed for the molybdenum complexes $[Mo_2(CO)_4(CHCHCMe_2)(C_5H_5)_2]$ (50), and $[Mo_2(CO)_2(CHCHCMe_2)(C_5H_5)O]$,(IV). The geometric changes observed between these allylidenes are smaller because the electronic imbalance at the two metals is also being tempered by a bridging carbonyl ligand which adopts different geometries.

The bonding of C_β and C_γ to the 'η^3-metal', M', appears to be less sensitive to electronic factors, though it is possible that steric requirements may influence the observed geometry. From Table 2.7 it can be seen that generally the metal-carbon bond lengths increase in the order

$$M-C_\alpha < M'-C_\alpha < M'-C_\beta < M'-C_\gamma$$

The geometry of the (μ-$CHCHCMe_2$) group for (VII) differs from that of most other μ-allylidene complexes with respect to the relative orientation of the substituents about the C_α-C_β bond. In (VII), H(9) and H(10) are in a trans geometry (possibly explaining the anomalously high H-H coupling constant). In compounds (50) and (IV) the equivalent atoms lie in a cis orientation.

An alternative description is to consider M' as bonded to a 1-metalla-allyl ligand in which the other metal may occupy a syn or an anti position. These would correspond to the trans and cis isomers, respectively.(see Fig 2.21)

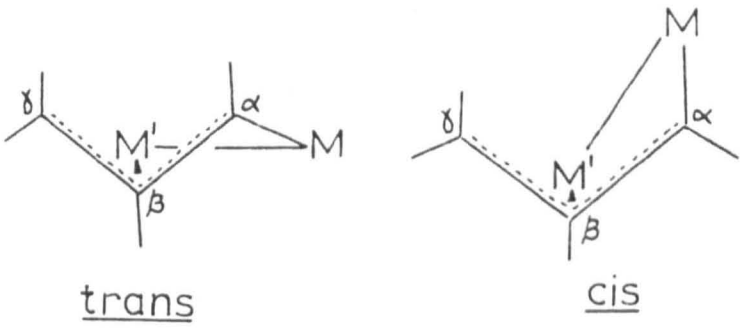


Figure 2.21

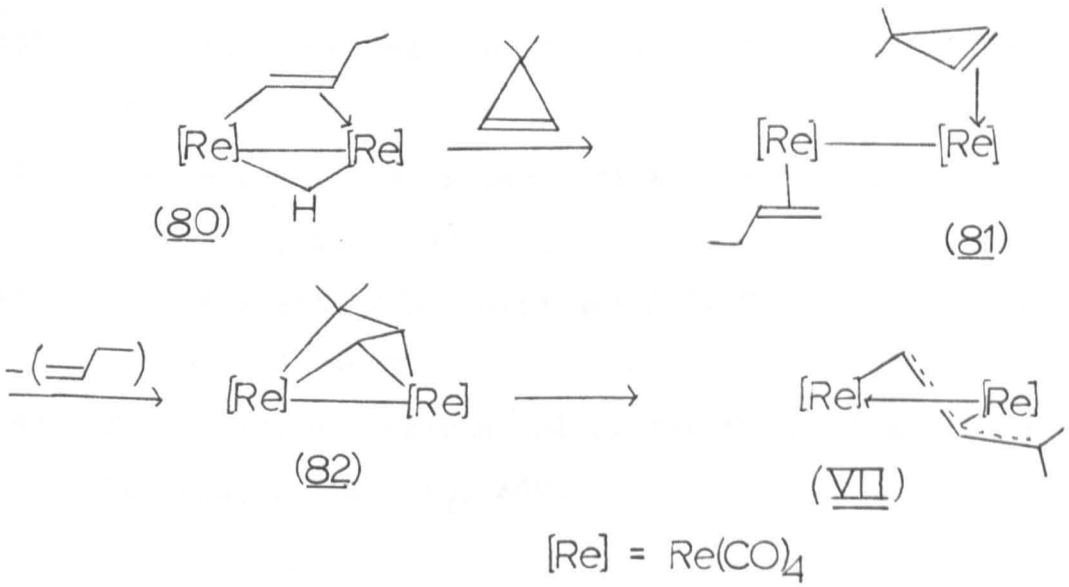
Of the other structurally characterised μ-allylidenes, only (53) appears to possess the trans geometry seen for (VII). This being

inferred from the molecular skeleton and torsion angles rather than by direct location of the hydrogen atoms.

The question of why these different isomers arise is of interest. So far the observation of a cis/trans isomerisation has not been reported. This would require conversion to a η^1-vinylcarbene, rotation about the C_α-C_β bond and recoordination of the vinyl group.

If interconversion is ruled out the the observation of different geometries for μ-allylidenes must be a consequence of the mechanism by which they are formed. In the case of (VII) it is likely that the intermediate (80) is involved, which upon dissociation of 1-butene would yield (81), which has a 16 electron Re centre. Instead of oxidative addition of the cyclopropene C-H bond it is possible that the metal adds across the ring-strained cyclopropene C_2-C_3 bond. This would give the complex (82). Compound (VII) would then be formed by a $\eta^2,\eta^2/\eta^1,\eta^3$ interconversion of the type seen by Herrmann et al. for (70).[111]

Scheme 2.12 Mechanism of Formation of (VII)



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Section 3.1

Experimental Details for Crystallographic Studies.

a) General Procedures

Preliminary Work

The important step of crystal selection was carried out with several criteria in mind. The air-sensitive nature of many of the complexes made microscopic examination difficult. Crystals were chosen which were representative of the batch in general, with well-defined faces, as equidimensional as possible, and with the exception of the dirhenium complex (VII) of Section 2 as large as was compatible with the size of the homogeneous X-ray beam. The absorption coefficients of most of the materials examined were on the order of 10 cm^{-1}, so that absorption effects did not limit intensity.

All crystals were mounted in Lindemann capillary tubes under a stream of dry nitrogen gas, they were secured by epoxy resin (or vacuum grease in the case of low temperature determinations) flame sealed and the tubes inserted in brass pins which allowed mounting on the goniometer.

Whenever possible preliminary photography on a Weissenberg camera was used to determine lattice symmetry, unit cell dimensions and check crystal singularity.

Data Collection

Intensity data were collected on a Nicolet P3m four-circle diffractometer, using graphite monochromated Mo-K_α

radiation. After optically centering the crystal a Polaroid rotation (ϕ) photograph was taken from which approximate angles for a number of reflections could be obtained. Refinement of these by an automatic scan procedure for up to 15 reflections was used to provide input to an auto-indexing routine. This took the three shortest non-coplanar reciprocal lattice vectors as a starting set and calculated linear combinations in real space, i.e. possible unit cell axes that were consistent with with other 12 reflections in the array.

Three axial solutions were picked which either agreed with preliminary photography or gave a cell of the highest lattice symmetry. In the absence of preliminary work axial photographs were taken on the diffractometer to confirm the axial lengths and check lattice symmetry.

Unit cell parameters were optimised by setting the angles of 15 reflections with high 2θ angles, (usually between 20 and 30°).

For low temperature studies a modified Nicolet LT-1 Low Temperature Attachment was used whereby a stream of cooled nitrogen gas was directed over the crystal.

Data were collected by either the moving crystal-moving counter method ($\theta/2\theta$ scans) or a moving crystal-stationary counter method (Wyckoff ω-scans), both in the bisecting mode, for which the χ-circle always lies between the collimator and the detector arm.

For the former scan technique, in which ω is driven at half the speed of 2θ, the peaks were measured in 96 steps,

the scan width typically 1.2° in 2θ either side of the K_{α_1} and K_{α_2} maxima. Variable scan rates were used, the speed being determined by a 2s prescan. Reflections with counts below a threshold C_{min} (typically 30 counts) were measured at the slowest scan speed S_{min}, usually 2.0° min^{-1} in 2θ, whereas reflections with intensity above a certain threshold C_{max} (1 500 counts) were measured at S_{max} 29.3° min^{-1} in 2θ. Other reflections with intermediate intensity were measured at rates interpolated from the above four settings.

At 2θ angles greater than 40°, a skip was employed so that reflections below the C_{min} threshold were not measured.

The background was measured at both ends of the scan, the ratio of total background:scan time was 0.5.

The Wyckoff ω-scan technique was employed for many of the data sets. Each peak was scanned in 13 steps (in ω) about the calculated diffraction maxima for K_{α_1} and K_{α_2}. If the observed peak maximum was too close to either end of the scan then additional scan steps (up to 6) were measured at that end. A background count was taken at a fixed point 1.0° either side of the peak. The total scan width could be varied to reflect crystal quality typically this was 1.0° in total.

Throughout data collection intensity standards were measured every 50 reflections to monitor crystal orientation and possible decay.

Data Reduction

Computation were carried out on a Data General Eclipse S/230 minicomputer using the SHELXTL package of X-ray programs.[1] The data was read from magnetic tape and processed by XTAPE this discarded reflections with asymmetric backgrounds, highly asymmetric or off-centred peaks and those reflections with more than 100,000 counts (above which intensity a correction for counter coincidence becomes unreliable). Correction was made for crystal decomposition after fitting a curve through the (averaged) intensities of the check reflections against exposure time. Lorentz and polarisation corrections were applied and direction cosines were calculated for use in absorption corrections. These latter were applied by two methods. The first was a numerical method based on accurate measurement of the crystal faces and using a Gaussian integration. The second was empirical, based on intensity measurements at different azimuthal angles (steps of 10° in χ) for a number of reflections and their symmetry equivalents. The variation of intensity for related measurements was used to refine 6 parameters which described a pseudo-ellipsoidal model of the crystal.

Processing of the raw data was then completed by discarding reflections which were absent due to space group extinctions and averaging those equivalent by symmetry.

Solution and Refinement

All structures were solved by conventional heavy atom methods. Positions of the metal atoms were obtained from

Patterson maps or by direct methods and used as phasing models for the location of the remaining non-hydrogen atoms from difference Fourier maps. Blocked cascade least squares refinement was employed, with a maximum of 103 parameters being refined in any given cycle.

For each structure, refinement was continued until convergence was reached, as evidenced by a stabilisation of the discrepancy indices to their final values. The maximum shift/esd for any parameter in the final cycle was also used as an indicator that refinement was complete, this value being typically 0.1 and with the average shift/esd for all parameters in the final cycle being on the order of 0.01.

In the final stages of refinement weighting schemes of the form $w = 1/[\sigma^2(F_o) + g F_o^2]$ were used, where $\sigma(F_o)$ is the standard deviation of F_o derived from counting statistics and w is the weight to be assigned to the reflection. The value of g, typically 0.0002, was chosen for each structure to give the least variation of the mean value of $w(|F_o|-|F_c|)^2$ over any subset of the reflections, based on index, parity group, sin θ and the magnitude of F_o.

The function minimised during refinement was

$$\sum w(|F_o|-|F_c|)^2$$

The effects of the weighting scheme were assessed in terms of the analysis of variance mentioned above, minimisation of the weighted and unweighted discrepancy indices, R and R_w, defined as:

$$R = \frac{\sum(||F_o|-|F_c||)}{\sum(F_o)} \qquad R_w = \frac{\sum w^{\frac{1}{2}}(||F_o|-|F_c||)}{\sum w^{\frac{1}{2}}(F_o)}$$

and an optimisation of the goodness of fit

$$GOOF = [\sum w(||F_o|-|F_c||)^2/n-m]^{\frac{1}{2}}$$

where n = no. of observations.

m = no. of least squares parameters.

to a value of unity.

Weak data were omitted from structure refinement, only those with $I > 2\sigma(I)$ being used.

The complex analytical scattering factors for neutral atoms of Cromer and Mann[2] were employed throughout.

Hydrogen atoms were routinely located but unless of chemical interest were not refined but given optimum geometries: d_{C-H} was set to 0.96 Å.

Details of the individual structure analyses are given below and Tables of bond lengths and angles and atomic positional and thermal parameters are presented in the Appendix.

Structure factor listings are available from the author.

Section 1: Experimental Details for Crystallographic Studies

Complex (I): Crystal Data: $C_{17}H_{33}BF_4MoO_6P_2$, M = 580.9, orthorhombic, space group Pcab, a = 16.352(3)Å, b = 17.475(3)Å, c = 17.543(3)Å, V = 5013(1)Å^3, z = 8, Dc = 1.54 gcm^{-3}, F(000) = 2447, μ(Mo-Kα) = 6.97cm^{-1}.

A deep purple needle of (I), dimensions (0.55 x 0.32 x 0.15 mm) was selected from a batch of crystals grown from CH_2Cl_2:hexane over a period of several days. 2616 unique observed reflections were measured in the range $3<2\theta<50^\circ$ over a period of 44hr at 293K. The systematic absences h0l: h = 2n+1, hk0: k = 2n+1, 0kl: l = 2n+1 indicated that the space group was Pcab, a non-standard setting of Pbca. The Patterson map revealed the position of one unique Mo atom; the 2x,2y,2z vector lying below a set of three vectors of relative multiplicity four; 2x+1/2,0,1/2, 1/2,2y+1/2,0 and 0,1/2,2z+1/2 and a further set of relative multiplicity two; 2x,1/2+2y,1/2, 1/2,2y,1/2+2z and 1/2+2x,1/2,2z. All non-hydrogen atoms were located by successive difference Fourier maps, and were refined with anisotrpic thermal parameters. Large thermal parameters were observed for the fluorines of the tetrafluoroborate anion indicating disorder of this group. Hydrogen atoms were fixed in ideal geometries (dC-H = 0.96Å) apart from the acetylenic hydrogen H(7) which was located and isotropically refined.

The final R = 0.056, Rw = 0.053 and the goodness-of-fit (GOOF) 1.646. The number of least squares parameters was 311 giving a data:parameter ratio of 8.4:1. No absorption correction was applied. The residual electron density maxima were located in the proximity of the

$[BF_4]$ group. The max was 0.9, the min 0.6 electrons$Å^{-3}$. The value of g used in the weighting scheme was 0.0003.

Complex (II): Crystal Data: $C_{20}H_{43}MoO_9P_3$, M = 616.4, monoclinic, space group $P2_1/c$, a = 11.731(3)Å, b = 12.796(3)Å, c = 18.827(4)Å, β = 92.33(2)°, V = 2824(1)$Å^3$, z = 4, Dc = 1.45 gcm-3, F(000) = 1288, μ(Mo-Kα) = 6.61cm^{-1}.

7734 independent reflection intensities were measured at 250K (θ-2θ scans, 2θmax = 65°) from a yellow data crystal of dimensions 0.55 x 0.5 x 0.35mm. Of these 7437 satisfied the criterion $I>2\sigma(I)$ and were used in structure refinement. Final residuals were R = 0.0262, Rw = 0.0263. The GOOF was 1.40. All non-hydrogen atoms were refined anisotropically, hydrogen atoms being given fixed geometries, excepting H(10) and H(11) which were isotropically refined. The value of g used in the weighting scheme was 0.0002. Residual electron density appeared mostly in the region about the Mo atom, no absorption correction being applied. The max/min values were +0.4, -0.6 e$Å^{-3}$. The number of refined parameters was 333 giving a data:parameter ratio of 22.5:1.

Complex (IV): Crystal Data: $C_{18}H_{32}MoO_7P_2$, M = 518.1, triclinic, space group $P\bar{1}$, a = 8.826(2)Å, b = 9.351(2)Å, c = 15.768(4)Å, α = 110.08(2)°, β = 93.19(2)°, γ = 110.64(2)°, V = 1120.5(5)$Å^3$, z = 2, Dc = 1.54 gcm^{-3}, F(000) = 536, μ(Mo-Kα) = 7.45cm^{-1}.

2167 unique observed reflections (ω-scans, 2θmax = 45°, room temp) were obtained from a data crystal of dimensions (0.4 x 0.35 x 0.3 mm).

Structure solution and refinement proceeded smoothly except for a problem of disorder for two arms of a trimethylphosphite ligand. This was modelled by assigning two positions to the methoxy oxygen atoms and refineing their site occupancies (to 0.56 and 0.44 for the major and minor components respectively). The P-O and O-CH_3 bond lengths were constrained to limits of chemically reasonable values. The final difference map revealed no residual electron density peaks > $\pm$1e$Å^{-3}$. No absorption correction was applied. All non-hydrogen atoms were anisotropically refined except for the disordered atoms O(5)A+B and O(6)A+B, which had isotropic thermal parameters. The data:parameter ratio was 7.8:1.

Complex (V): Crystal Data: $C_{26}H_{36}MoO_6P_2$, M = 602.1, monoclinic, space group $P2_1/c$, a = 13.499(7)Å, b = 10.452(3)Å, c = 19.623(9)Å, β = 97.72(4)°, V = 2744(2)$Å^3$, z = 4, Dc = 1.45 gcm^{-3}, F(000) = 1248, μ(Mo-Kα) = 6.17cm^{-1}.

Red crystals of (V) were grown from toluene at -30°c, as hexagonal plates. Difficulty was encoutered in obtaining a unit cell. These were found to be twinned upon examination under polarised light. Cleavage of one crystal in half yielded a single crystal fragment of dimensions 0.5 x 0.3 x 0.1 mm. This was used for the collection of 2994 unique observed reflections (2θmax = 50°, ω-scans, 297K). Final discrepancy indices were R = 0.034, Rw = 0.032, with GOOF = 1.323, g = 0.0002. Residual electron density was +0.6, -0.3e$Å^{-3}$ and the data:parameter ratio 8.9:1.

Complex (VI): Crystal Data: $C_{17}H_{34}MoO_6P_2$, M = 492.1, triclinic, space group $P\bar{1}$, a = 9.660(1)Å, b = 11.978(1)Å, c = 19.578(4)Å, α = 91.38(1)°, β = 94.25(1)°, γ = 93.48(1)°, V = 2253.9(5)Å^3, z = 4, Dc = 1.45 gcm^{-1}, F(000) = 1024, μ(Mo-Kα) = 7.33 cm-1.

A pale yellow crystal of dimensions 0.5 x 0.55 x 0.2 mm was used to collect 7816 unique observed reflections (θ/2θ scans, 250K, 2θmax = 55°). The structure was solved by the heavy atom method. The Patterson map revealed the positions of two unique molybdenum atoms found to be derived from two crystallogaphically independent molecules of (V). The solution refined to final values for R and Rw of 0.026 and 0.027 respectively. All non-hydrogen atoms were anisotropically refined, the hydrogens were given ideal geometries and constrained to ride on their carbon atoms except for the methylene hydrogens H(8A), H(8B), H(25A) and H(25B) which were located in a difference Fourier map and isotropically refined. The GOOF was 1.369 and the value of g = 0.0002. There were 621 least-squares parameters giving a data:parameter ratio of 12.6:1. Residual electron density was +1.1, -0.7eÅ^{-3}. An absorption correction was applied based on the assignment of the indices [1,0,0], [1,1,0] and [0,0,1] to the crystal faces. This resulted in a decrease of R from 0.029 to its final value.

Complex (VII): Crystal Data: $C_{20}H_{36}MoO_6P_2Si$, M = 558.1, triclinic, space group $P\bar{1}$, a = 10.145(3)Å, b = 10.446(3)Å, c = 15.384(6)Å, α = 101.85(3)°, β = 97.66(3)°, γ = 122.85(2)°, V = 1279.7(7)Å3, z = 2, Dc = 1.45 gcm^{-3}, F(000) = 580, μ(Mo-Kα) = 6.99cm^{-1}.

A green crystalline block of dimensions 0.5 x 0.4 x 0.15 mm was

sealed in a capillary tube under an atmosphere of dry argon and stored at -30°c. Upon transfer to the diffractometer it was cooled further over a period of 30min to -50°c, at which temperature the crystal was stable to x-ray exposure and data were collected (ω-scans, 2θmax = 45°, 32hrs). 2830 unique observed reflections were used in structure solution and refinement. Final discrepancy indices of R = 0.026, Rw = 0.026 were obtained. Non-hydrogen atoms were anisotropically refined, the hydrogens H(8A) and H(8B) were refined isotropically. The GOOF was 1.32 for g = 0.0002. Residual electron density was not significant; $\pm$0.5eÅ^{-3}. The data:parameter ratio was 9.25:1.

Complex (VIII): Crystal Data: $C_{17}H_{35}BF_4MoO_6P_2$, M = 580.0, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), a = 9.440(2)Å, b = 15.012(5)Å, c = 18.135(6)Å, β = 103.97(2)°, V = 2494(1)Å^3, z = 4, Dc = 1.55 gcm^{-3}, F(000) = 1192, μ(Mo-Kα) = 6.96cm^{-1}.

A colourless crystal of dimensions 0.6 x 0.55 x 0.5 mm was mounted under dry nitrogen in a glass capillary tube. This was of good quality (peak widths at half height were < 0.25° in ω) and was used for data collection (θ-2θ scans, 250K, 2θmax = 50°, 131hrs). Solution and refinement of the structure proceeded smoothly to R = 0.0223, Rw = 0.0237, with all non-hydrogens anisotropic. The terminal hydride H and the hydrogens of the carbyne β-carbon H(8A) and H(8B) were freely refined with isotropic thermal parameters. An empirical absorption correction based on azimuthal scan data was successfully applied (R was lowered by 0.0025). The GOOF was 1.776 for g = 0.0001. Residual electron density had max and min values of $\pm$0.5eÅ^{-3} and the data:parameter ratio

was 15.8:1.

Complex (IX): Crystal Data: $C_{15}H_{24}F_6MoO_{10}P_2$, M = 636.2, monoclinic, space group $P2_1/c$, a = 8.496(5)Å, b = 13.911(9)Å, c = 19.527(13)Å, β = 90.13(5)°, V = 2308(3)Å^3, z = 4, Dc = 1.51 gcm^{-3}, F(000) = 1280, μ(Mo-Kα) = 7.78cm^{-1}.

An orange-red crystal of dimensions 0.25 x 0.16 x 0.14 mm was used to collect 2483 unique observed reflections (θ-2θ scans, 2θmax = 50°, 250K, 124hrs). The molybdenum position was obtained from a Patterson map and used as a phasing model. Refinement of the structure didnot proceed smoothly to completion, as disorder of a trifluoroacetate moiety was discovered. This was refined in two conformations with partial occupancies of 0.68 and 0.32, with the atoms F(4) and C(10) common to both major and minor components. All non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of the atoms of the minor [CF_3CO_2] conformer. Final discrepancy indices were R = 0.075, Rw = 0.070. For g = 0.00025 GOOF = 2.14. Residual electron density had a maximum of +1.8eÅ^{-3} in the region of the metal and other peaks >1eÅ^{-3} were seen in the proximity of the disordered ligand. The minimum was -1.1eÅ^{-3}. An absorption correction was applied based on a model of the crystal bounded by the faces {[0,1,2],[0,-1,-2](0.14mm)}, {[0,1,-1],[0,-1,1](0.16mm)} and {[1,0,0],[-1,0,0](0.25mm)}. This did not appreciably improve refinement of the structure, however. The data:parameter ratio was 7.4:1.

Complex (X): Crystal Data: $C_{20}H_{25}MoN_4O_3P$, M = 496.1, orthorhombic, space group $P2_12_12_1$, a = 9.221(2)Å, b = 14.587(3)Å, c = 17.175(4)Å, V = 2310.2(8)Å^3, z = 4, Dc = 1.43 gcm^{-3}, F(000) = 1016, μ(Mo-Kα) = 6.47cm^{-1}.

Data was collected on a colourless crystal (0.6 x 0.5 x 0.35mm) at room temperature (ω-scans, 2θmax = 65°, 25hrs). 2510 unique reflections were observed and used in structure solution and refinement to which disorder of two arms of the [P(OMe)$_3$] ligand posed the only problem. The oxygen atoms of these two methoxy groups were each refined in two positions of site occupancy 61 and 39%. Final R and Rw were 0.036 and 0.038 respectively. The GOOF was 1.73 for g = 0.0002. Residual electron density peaks no greater than $\pm$0.8eÅ^{-3} were observed in the final difference map. No absorption correction was attempted. The number of least-squares parameters was 280 (non-hydrogen atoms anisotropic apart from O(2A), O(2B), O(3A) and O(3B) of the disordered ligand) giving a data:parameter ratio of 9.0:1. A check of the absolute configuration of the complex by consideration of anomalous scattering confirmed the assignment used.

Complex (XI): Crystal Data: $C_{23}H_{34}F_{12}MoO_8P_2$, M = 824.1, triclinic, space group P$\bar{1}$, a = 9.935(2)Å, b = 20.643(8)Å, c = 18.016(6)Å, α = 91.91(3)°, β = 111.92(2)°, γ = 82.97(2)°, V = 3402(2)Å , z = 4, Dc = 1.61 gcm^{-3}, F(000) = 1688, μ(Mo-Kα) = 5.72cm^{-1}.

4100 unique observed reflections were collected (ω-scans, 2θmax = 50°, 57 hrs, room temp.) on a large pale yellow crystal (0.65 x 0.5 x 0.4mm). The structure was solved by the heavy atom method. The Patterson

synthesis yielding positions for two molybdenum atoms in the asymmetric unit (i.e. z = 4).The final discrepancy indices were R = 0.0442, Rw = 0.0468 with a GOOF of 1.243 for g = 0.00015. No residual electron density peaks greater than $\pm 0.6 e\text{Å}^{-3}$ were found in the final differnce map, although no correction for absorption was attempted.

Complex (XII): Crystal Data: $C_{17}H_{33}IMoO_6P_2$, M = 618.0, monoclinic, space group $P2_1/c$, a = 10.362(3)Å, b = 14.293(4)Å, c = 16.576(3)Å, β = 102.70(2)°, V = 2395(1)Å^3, z = 4, Dc = 1.71 gcm^{-3}, F(000) = 1232, μ(Mo-Ka) = 19.7cm^{-1}.

A large red data crystal (0.75 x 0.25 x 0.3mm) was used to collect 5110 unique observed reflections ($\theta/2\theta$-scans, 250K, $2\theta max$ = 65°, 111 hrs). Positions for both Mo and I were obtained from the Patterson map and used for solution of the structure. Refinement was to R = 0.044, Rw = 0.045 with a GOOF of 2.40 for g = 0.0002. Peaks of significant electron density $\pm 2.0 e\text{Å}^{-3}$ were located in the vicinity of the heavy atoms (Mo,I) inspite of an empirical absorption correction. A peak ($0.75 e\text{Å}^{-3}$) was assigned to the β-hydrogen of the vinylidene ligand and refined isotropically. All non-hydrogen atoms were anisotropically refined giving 248 l.s. parameters and a data:parameter ratio of 20.6:1.

Complex (XIII): Crystal Data: $C_{17}H_{34}BF_4IMoO_6P_2$, M = 705.8, orthorhombic, space group $P2_12_12_1$, a = 9.281(8)Å, b = 15.89(1)Å, c = 18.04(1)Å, V = 2661(4)Å3, z = 4, Dc = 1.76 gcm^{-3}, F(000) = 1400, μ(Mo-Kα) = 18.03cm^{-1}.

Low quality of the x-ray data due to crystal fracture allowed convergence to only R = 0.20. (for 1286 reflections, 250K, ω-scans, $2\theta max = 50°$). Further refinement was not attempted after all non-hydrogen atoms were located.

Complex (XIV): Crystal Data: $C_{19}H_{29}BrMoO_6P_2$, M = 519.0, monoclinic, space group $P2_1/c$, a = 9.749(7)Å, b = 14.773(9)Å, c = 16.834(9)Å, β = 101.34(5)°, V = 2.377(3)Å^3, z = 4, Dc = 1.65 gcm^{-3}, F(000) = 1192, μ(Mo-Kα) = 23.7cm^{-1}.

A red-brown crystal of irregular shape (approx. 0.6 x 0.4 x 0.33 mm) was used in the collection of 3 078 unique observed reflections (ω-scans, 42 hrs, 298 K, $2\theta max = 50°$) Refinement was to R = 0.0463 R_w = 0.0468, with a GOOF of 1.43 (g 0 0.0007). An empirical absorption correction was applied (max/min transmition factors were 0.83/0.65). Residual electron density was +1.5, -1.0 eÅ^{-3}, with the maximum 1.08 Å from the molybdenum.

Disorder of two methoxy groups was modelled by defining two positions for the oxygen atoms (04A, 04B) and (06A, 06B) and using common methyl carbon (C4, C6). Constraints of 1.60(2) and 1.43(2) Å were placed on the P-O and O-C bond lengths of the disordered moiety. The number of least squares parameters was 293 giving a data:parameter ratio of 10.3:1.

Experimental Details for Crystallographic Studies for Section 2

Complex (I): Crystal Data: $C_{24}H_{28}Mo_2O_3.(CH_2Cl_2)$, M = 556.2(641.1), monoclinic, space group $P2_1$ (No.4), a = 8.745(5)Å, b = 14.571(7)Å, c = 10.909(4)Å, β = 112.87(3)°, V = 1281(1)Å^3, z = 2, Dc = 1.66gcm^{-1}, F(000) = 444, μ(Mo-Kα) = 11.64cm^{-1}.

A deep green crystal of dimensions 0.4 x 0.3 x 0.12mm was used for data collection (36hrs). 3228 unique observed reflections were measured in the range $3<2\theta<60°$ at 293K using the ω-scan technique. The sharpened Patterson map revealed positions for two independent Mo atoms. However because the space-group was the non-centrosymmetric $P2_1$, the accidental near-equivalence of the y-coordinates of these caused the Fourier maps to have pseudo-mirror symmetry. Eventually all atomic positions were located and refinement then proceeded smoothly to R = 0.0308, Rw = 0.0348. The GOOF was 1.263 for a value of g = 0.00063 in the weighting scheme. Residual electron density was +1.0, -0.6eÅ^{-3}. The largest positive residual peaks were associated with thhe molybdenum atoms and could be attributed to absorption, no correction having been applied. Apart from these, the maximum residual electron density was <0.3eÅ^{-3}. All non-hydrogen atoms were anisotropically refined with H(8), H(9) and H(10) being the only hydrogen atoms freely refined. The number of least-squares parameters was 318 yielding a data:parameter ratio of 10.2:1.

Complex (II): Crystal Data: $C_{24}H_{25}Mo_2O_5$, M = 584.1, triclinic, space group $P\bar{1}$ (No.2), a = 8.591(2)Å, b = 8.906(3)Å, c = 15.071(4)Å, α = 89.10(2)°, β = 99.65(2)°, γ = 99.06(2)°, V = 1169.5(6)Å^3, z = 2, Dc = 1.66gcm^{-3}, F(000) = 584, μ(Mo-Kα) = 10.77cm^{-1}.

A Dark redplate (0.4x0.3x0.05mm) of good quality (peak width at half height <0.3° for ω-scans) was used in the collection of 3543 unique observed reflections (ω-scans, 2θmax = 50°, 293K, 43 hrs). Structure solution proceeded smoothly to R = 0.0329, Rw = 0.0338 with GOOF = 1.231. Non-hydrogen atoms were given anisotropic thermal parameters. H(6) and H(7) were the only hydrogen atoms freely refined. There were 300 l.s. parameters, the data:parameter ratio being 11.8:1. No absorption correction was applied, the residual electron density being +0.7,-0.9eÅ^{-3}. A (refined) value of 0.00051 was used for g in the weighting scheme.

Complex (III): Crystal Data: $C_{22}H_{22}Mo_2O_4$, M = 542.1, monoclinic, space group $P2_1/c$, a = 10.731(1)Å, b = 14.652(3)Å, c = 14.655(1)Å, β = 110.972(8)°, V = 2151.5(5)Å^3, z = 4, Dc = 1.67gcm^{-1}, F(000) = 1080, μ(Mo-Kα) = 11.61cm^{-1}.

An orange-red crystal (0.5 x 0.3 x 0.2mm) was used to collect 3927 unique observed reflections (ω-scans, 2θmax = 55°, 43hrs, 293K). The structure was refined to R = 0.0261, Rw = 0.0272, (GOOF = 1.30, g = 0.0002). Only the methyl and cyclopentadienyl hydrogen atoms were fixed, the others being located and positionally refined. All non-hydrogen atoms were anisotropically refined. An empirical absorption correction was applied. Sets of equivalent reflections were scanned at different

azimuthal settings (ψ-scans). The max/min transmission factors were 0.80/0.72. The final difference map was clean, residual electron density being +0.3,-0.5eÅ^{-3}. The number of least-squares parameters was 283, giving a data:parameter ratio of 13.9:1.

Complex (IV): Crystal Data: $C_{17}H_{18}Mo_2O_3$, M = 462.1, monoclinic, space group $P2_1/n$, $\underline{a}$ = 7.4734(9)Å, $\underline{b}$ = 12.123(2)Å, $\underline{c}$ = 18.073(3)Å, β = 92.87(1)°, V = 1635.4(4)Å^3, z = 4, D_c = 1.88gcm^{-3}, F(000) = 912, μ(Mo-Kα) = 15.06cm^{-1}.

A deep-red data crystal of dimensions 0.5 x 0.45 x 0.15mm was used to collect 3055 unique observed reflections in the range $3< 2\theta< 55°$ (293K, 33 hrs) by the ω-scan method. Solution of the Patterson map was straightforward, however it became clear that one of the cyclopentadienyl rings was affected by rotational disorder. Two fixed ring positions were therefore defined and their occupancies refined. At a later stage the geometrical constraints were lifted and the carbon atoms of both rings refined with anisotropic thermal parameters. The final site occupancies were 52/48%. It also became apparent that reflections with large F were systematically weaker than their calculated values, for those reflections with the greatest Δ/σ. This indicated that extinction might be occurring to a significant extent. The high quality of the crystal (peak widths at half-height were < 0.25° in ω) was the probable cause of this . Accordingly an extinction parameter was refined which reduced this effect empirically.

Final R and Rw values of 0.0252 and 0.0258 were attained. The GOOF was 1.10 for g = 0.0003. Residual electron density was not > ±0.5 eÅ^{-3}.

The number of least squares parameters was 210 giving a data:parameter ratio of 14.6:1.

Complex (V): Crystal Data: $C_{24}H_{20}Mo_3O_4$, M = 660.1, monoclinic, space group $P2_1/n$, a = 8.066(1)Å, b = 17.557(5)Å, c = 15.754(5)Å, β = 101.35(2)°, V = 2187(1)Å^3, z = 4, D_c = 2.00gcm^{-1}, F(000) = 1288, μ(Mo-Ka) = 16.8cm^{-1}.

2888 unique observed reflections were measured over a 30 hr period from a dark green crystal (0.45 x 0.4 x 0.15mm). The ω-scan technique was used, no significant decay was observed at 297K. The structure was refined to R = 0.026. All hydrogen atoms were directly located, though only H(6) and H(19) were freely refined.

The GOOF was 1.38 for g = 0.0002 (refined value).. Residual electron density was at the ±0.6 eÅ^{-3} level. The number of least squares parameter was 291, giving a data parameter ratio of 10.0:1.

Complex (VI): Crystal Data: $C_{27}H_{38}O_2Rh_2$, M = 600.1, monoclinic, space group $P2_1/c$, a = 14.544(7)Å, b = 9.280(5)Å, c = 19.258(8)Å, β = 102.28(4)°, V = 2540(2)Å^3, z = 4, Dc = 1.57gcm^{-3}, F(000) = 1224, μ(Mo-Kα) = 12.99cm^{-1}.

Thee red data crystal of (VI) (dimensions 0.6 x 0.55 x 0.2 mm) was cooled to 250K and 3201 unique observed reflections were measured in the range 3< 2θ< 50°, over 46 hrs using the ω-scan technique. The structure refined to R = 0.0505, Rw = 0.0516, with a GOOF of 1.596. Hydrogen atoms were fixed except for H(3) and H(7) which were isotropically refined.

A weighting scheme with g = 0.0008 was applied. 324 l.s. parameters were used giving a data:parameter ratio of 9.9:1. No absorption correction was applied. The residual electron density had maxima and minima on the order of 2.0eÅ^{-3}, these were associated with the rhodium atoms.

Complex (VII): Crystal Data: $C_{13}H_8O_8Re_2$, M = 664.6, monoclinic, space group $P2_1/c$, a = 8.576(3)Å, b = 9.872(7)Å, c = 19.623(10)Å, β = 99.54(3)°, V = 1607Å^3, z = 4, Dc = 2.75gcm^{-3}, F(000) = 1200, μ(Mo-Kα) = 153.0cm^{-1}.

2314 reflections were collected from the yellow data crystal(0.5x0.4x0.2mm) at 297K (ω-scans, 24 hrs, 2θmax = 50°) and used for solution and refinement. Final discrepancy indices were R = 0.0415, Rw 0.0422 and GOOF = 1.457. A wieghting factor g = 0.00075 was used. An empirical absorption correction was applied. The optimum value of μr was 0.35, for which the Rmerge of the azimuthal scan data was dropped to 0.0698 from 0.1988. Max/min transmision factors were 0.735 and 0.205. Application of this to the data set reduced R by 4.2%. Residual electron density was still at the 2.0eÅ^{-3} level, however, these peaks being centered around the rhenium atoms. An extinction parameter was again refined. Hydrogen atoms were given fixed geometries, with the exception of H(9) and H(10) which were refined freely. The number of l.s. parameters was 223 giving a data:parameter ratio of 10.4:1.

Section 3.2

Experimental

Synthetic Procedures

All experiments were carried out in an inert atmosphere of dry, oxygen-free nitrogen. Manipulation of the compounds was by conventional Schlenk line techniques.

Dry, degassed solvents were obtained by distillation, in a nitrogen atmosphere, over the following reagents: sodium/benzophenone (diethyl ether and tetrahydrofuran), sodium (pentane and hexane) and P_2O_5 (methylene chloride).

Characterisation

Unless stated otherwise, ^{1}H and ^{13}C n.m.r. spectra were recorded on a JEOL FX200 F.T. n.m.r. spectrometer. The ^{31}P n.m.r. spectra were recorded on a JEOL FX90Q n.m.r. spectrometer.

N.m.r. solvents were degassed by carrying out the freeze-thaw-pump cycle several times prior to use.

Chemical shifts are quoted in p.p.m. on the δ scale and are relative to $SiMe_4$ which was used as an internal standard for the ^{1}H and ^{13}C nuclei. The ^{31}P shifts are given relative to H_3PO_4 (external standard).

Infra red spectra were obtained on a Perkin-Elmer 457 grating spectrometer. Mass spectra were recorded on an A.E.I. MS902 mass spectrometer operating at 70 eV..

Microanalyses for C, H and N were carried out by the Microanalytical Laboratory of the School of Chemistry.

Preparative Details and Spectroscopic Data for Section 1

The preparation of the compounds $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (I), $[Mo(\eta^1\text{-}CH{=}CHBu^t)\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]$, (II), $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, (VI), and $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (VIII) has been reported in detail elsewhere.[3,4]

Additional spectroscopic details for (VIII) are given below.

Data for the compounds $[Mo{=}C(Me)CPh_2\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, (V) and $[Mo{=}C(SiMe_3)CH_2\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$, (VII), are given in the Ph.D. Thesis of S.R. Allen,[5] and for $[Mo(C{=}CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)Br]$, (XII), in the Ph.D. Thesis of R.G. Beevor.[6] A report of the chemistry of the acetylide complex (IV) $[Mo(CO)(C{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ has also been submitted in the B.Sc. Thesis of K. Primrose.[7]

a) Reaction of (I) with $K[BHBu^s_3]$ and (CO).

A purple slurry of $[Mo(HC{\equiv}CBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (I), (2.0 g, 3.5 mmol) in 50 ml THF was purged with (CO) gas for 10-15 min. The reaction vessel was cooled to -78 °C by an acetone/dry ice bath and potassium selectride^R, $K[BHBu^s_3]$ was added dropwise (as a 1 M solution in THF) in slight excess (4 ml). Carbon monoxide was continuously bubbled through as the solution was slowly brought to room temperature (30 mins). During this time the colour of the solution changed to an orange-brown. Removal of solvent, followed by extraction with hexane (4 x 20 ml) and

column chromatography on alumina, yielded (hexane/ether fraction) yellow crystalline (IV) $[Mo(CO)(C{\equiv}CBu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$, contaminated by (III), $[Mo(CO)(\eta^1\text{-}CH{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (approx. 15 %). Total yield was 600 mg (approx. 30 %). Repeated columning/recrystallisation enabled the isolation of pure (IV).

Data for (IV):

Colour: Yellow

Solubility: Hexane

N.m.r. Spectra

^1H: (C_6D_6), 5.07 (t, 5 H, $C_5\underline{H}_5$, $^3J_{P-H}$ = 1.5 Hz), 3.62 (virtual t, 18 H, $\{P(O\underline{CH}_3)_3\}_2$, J = 11.2 Hz), 1.26 (s, 9 H, $C(\underline{CH}_3)_3$).

$^{13}C\text{-}\{^1H\}$: (C_6D_6) 255.8 (t, Mo—$\underline{C}{\equiv}O$, $^2J_{P-C}$ = 42 Hz), 154.3 (t, Mo—$C{\equiv}\underline{C}$, $^3J_{P-C}$ = 7 Hz), 124.3 (t, Mo—$\underline{C}{\equiv}C$, $^2J_{P-C}$ = 45 Hz), 90.1 (s, $\underline{C}_5H_5$), 52.9 (s, $\{P(O\underline{CH}_3)_3\}_2$), 37.4 (s, $\underline{C}(CH_3)_3$), 32.4 (s, $C(\underline{CH}_3)_3$).

^{31}P n.m.r.: 49.9 singlet.

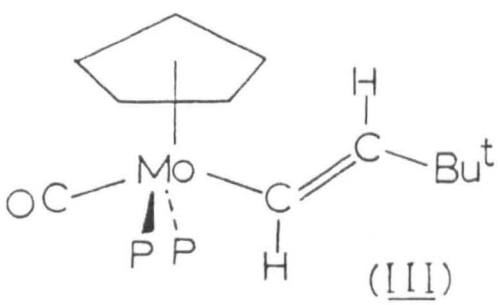
Infra Red Spectrum: (Hexane)

Range (2 200- 1 700 cm^{-1}) 1 875 (s), 1 855 (s) cm^{-1}, $\nu(C{\equiv}C)$, $\nu(C{\equiv}O)$.

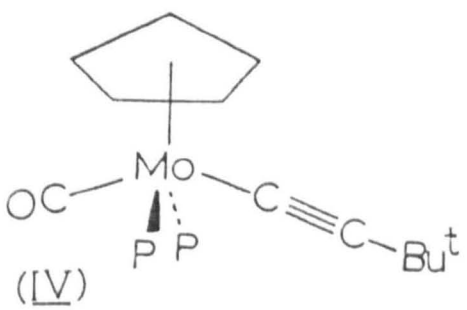
Mass Spectrum: m/e = 520 (M^+), m/e = 489 (M^+—OCH_3), m/e = 124 ($P(OMe)_3^+$).

Analysis

	C	H
Calc. (%)	41.54	6.54
Found (%)	41.84	6.29



(III)



(IV)

Data for (IV): trans-[Mo(CO)(η^1-(E)-CH=CHBu^t){P(OMe)$_3$}$_2$(C_5H_5)].

Colcur: (Yellow) Solubility: Hexane

N.m.r. Spectra:

^{1}H: (C_6D_6) 6.53 (dt, 1 H, Mo—CH=CH, $^3J_{P-H}$ = 9 Hz, $^3J_{H-H}$ = 18 Hz), 5.58 (dt, 1 H, Mo—CH=CH, $^4J_{P-H}$ = 3.5 Hz, $^3J_{H-H}$ = 18 Hz), 5.08 (s, 5 H, C_5H_5), 3.47 (virtual t, 18 H, {P(OCH$_3$)$_3$}$_2$, J = 11.2 Hz), 1.15 (s, 9 H, C(CH$_3$)$_3$).

^{13}C-{^{1}H}: (C_6D_6), 91.3 (s, C_5H_5), 52.0 (s, P(OCH$_3$)$_3$ $_2$), 30.3 (s, C(CH$_3$)$_3$). Signals for the other carbon atoms were not detected.

^{31}P-{^{1}H}: 49.9, singlet.

Other analytical data are unavailable as the compound was observed only as an impurity in the sample of (IV).

Reaction of (VI) with HBF_4.

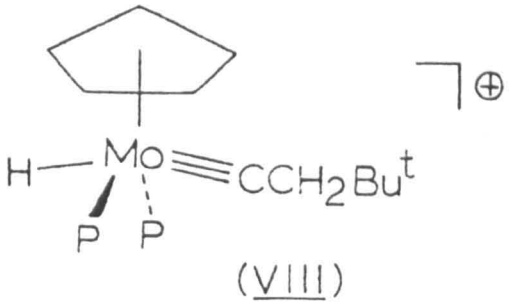
The procedure followed was exactly as described by Bottrill.[3] The product (VIII), $[H(Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ is air and moisture sensitive, though stable to exposure to air for short periods of time in the solid state. Attempts to form (VIII) on treatment of (VI) by dropwise addition of $[HBF_4.Et_2O]$ at -78 °C in Et_2O did not yield a pure product; the colourless complex (VIII) was contaminated by a red oily material.

Recrystallisation of pure (VIII) by layer diffusion of hexane into a methylene chloride solution of (VIII) at -30 °C gave large, X-ray quality crystals over a period of days.

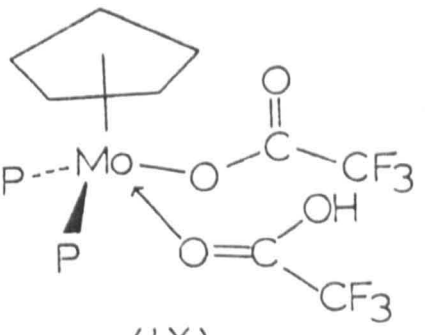
Additional Data for (VIII):

^1H: ($CDCl_3$) 5.75 (s, 5 H, $C_5\underline{H}_5$), 3.77 (virtual t, 18 H, $\{P(O\underline{CH}_3)_3\}_2$, J = 12.1 Hz), 2.39 (dt, 2 H, $\underline{CH}_2$, $^4J_{H-H}$ = 1.5 Hz, $^4J_{P-H}$ = 3.6 Hz), 1.03 (s, 9 H, $C(\underline{CH}_3)_3$), -2.60 (tt, 1 H, Mo-$\underline{H}$, $^2J_{P-H}$ = 66.7 Hz, $^4J_{H-H}$ = 1.5 Hz)

^{13}C: ($CDCl_3$) 346.4 (dtt, Mo$\equiv\underline{C}$, $^2J_{P-C}$ = 33.2 Hz, $^2J_{C-H}$ = 5.9 Hz, $^2J_{C-H}$ = 6.4 Hz). 96.4 (m, $\underline{C}_5H_5$, $^1J_{C-H}$ = 175 Hz, $^{2\text{-}3}J_{C-H}$ = 6.7 Hz), 64.5 (dt, $^1\underline{CH}_2Bu^t$, $^1J_{C-H}$ = 125 Hz, $^3J_{C-H}$ = 4.3 Hz), 53.7 (dq, $\{P(O\underline{CH}_3)_3\}_2$, $^1J_{C-H}$ = 134 Hz, $^2J_{C-P}$ = 6 Hz), 33.8 (s, $\underline{C}(CH_3)_3$), 29.4 (q, $C(\underline{CH}_3)_3$, $^1J_{C-H}$ = 115 Hz).



(VIII)



(IX)

Reaction of (VI) with CF_3COOH:

To a stirred solution of 300 mg (0.6 mmol) of (VI) in 10 ml of Et_2O was added 5 ml of a 10 % solution of CF_3COOH (i.e. excess) in Et_2O at -78 °C. The solution immediately changed colour from yellow to deep orange. Solvents were removed giving a red/orange oil. This was washed with pentane (2 x 10 ml), taken up in Et_2O (10 ml) and the volume of the solution reduced, whereupon a pale orange precipitate began to form. The resulting solid was dissolved in 5 ml CH_2Cl_2 and a layer of pentane (20 ml) allowed to diffuse into this at 0 °C. Rod-shaped crystals of (IX) were produced (120 mg, 40 % yield).

Data for (IX): $[Mo\{P(OMe)_3\}_2(CF_3CO_2H)(OCOCF_3)(\eta\text{-}C_5H_5)]$.

Colour: Orange-red Solubility: Ether(slight) CH_2Cl_2

N.m.r. Spectra

^1H: $C_6D_5CD_3$) 7.67 (t, 1 H, $CF_3COO\underline{H}$, J_{P-H} = 77.8 Hz), 5.30 (t, 5 H, $C_5\underline{H}_5$, $^3J_{P-H}$ = 3 Hz) 3.39 (virtual t, 18 H,

$\{P(O\underline{C}H_3)_3\}_2$, J = 10.8 Hz).

$^{13}C-\{^1H\}$: ($C_6D_5CD_3$) 98.6 (s, $\underline{C}_5H_5$), 53.5 (s, $\{P(O\underline{C}H_3)_3\}_2$).

$^{31}P-\{^1H\}$: ($C_6D_5CD_3$) 168.4, s

Analysis

	C	H
Calc. %	28.30	3.77
Found %	27.19	3.86

Reaction of (VI) with TCNE:

To a CH_2Cl_2 (15 ml) solution of (VI) (500 mg, 1 mmol) was added 150 mg of solid TCNE (Caution!) (1.1 mmol) at room temperature. Instantaneous reaction occurred, the colour of the solution turning deep-green. Column chromatography on alumina gave a fast green band and a pale pink band in CH_2Cl_2. The green species was unstable, yielding colourless crystals of (X) from CH_2Cl_2/hexane at 0 °C. The material from the pink fraction also proved to be (X). Attempts to characterise the green species were unsuccessful; the ^1H n.m.r. of a solution ($CDCl_3$) which was still green showed essentially only resonances for (X).
Total yield of (X) was 220 mg (45 %).

Data for (X): $[Mo\{\eta^2-C_2(CN)_4\}(CCH_2Bu^t)\{P(OMe)_3\}(\eta-C_5H_5)]$.

Colour: Very pale pink Solubility: CH_2Cl_2

N.m.r. Spectra:

^1H: (90 MHz) ($CDCl_3$) 5.77 (s, 5 H, $C_5\underline{H}_5$), 3.99

(d, 9 H, $P(OCH_3)_3$, $^3J_{P-H}$ = 11.4 Hz), 2.40 (d, 1 H, $^4J_{P-H}$ = 4.8 Hz, $CC\underline{H}_2Bu^t$), 2.34 (d, 1 H, $^4J_{P-H}$ = 6.6 Hz, $CC\underline{H}_2Bu^t$), 1.04 (s, 9 H, $C(C\underline{H}_3)_3$).

$\underline{^{13}C-\{^1H\}}$: ($CDCl_3$) 338.9 (d, Mo≡C, $^2J_{P-C}$ = 31.8 Hz), 118.3 (s), 116.8 (s), 116.3 (s), $\underline{C}_2(\underline{C}N)_4$, 101.9 (s, $(\underline{C}_5H_5)$), 63.3 (s, $\underline{C}H_2Bu^t$), 55.2 (d, $\{P(O\underline{C}H_3)_3\}$, $^2J_{P-C}$ = 7.3 Hz), 34.2 (s, $\underline{C}(CH_3)_3$), 29.7 (s, $C(\underline{C}H_3)_3$.

$\underline{^{31}P-\{^1H\}}$: ($CDCl_3$) 157.1 (s).

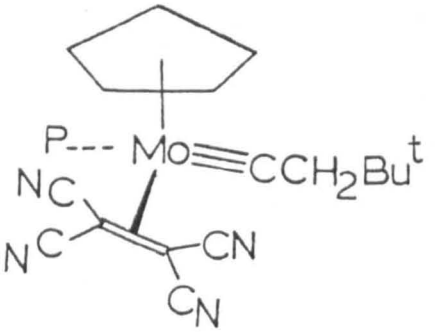
Infra Red Spectrum: (CH_2Cl_2)

Range: 2 400-1 700 cm^{-1} 2 222 cm^{-1}, $\nu(C\equiv N)$

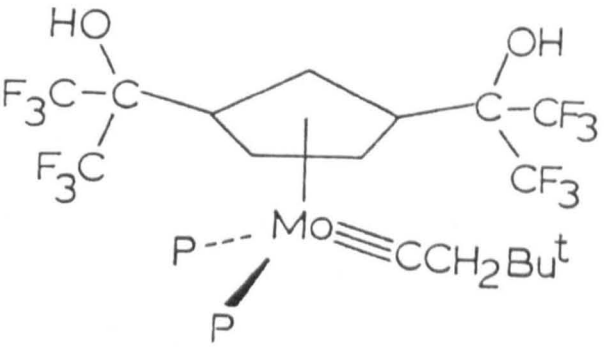
Mass Spectrum: m/e = 496 (M^+), m/e = 368 ($M-\{C_2(CN)_4\}^+$)

Analysis

	C	H	N
Calc. %	48.29	5.03	11.26
Found %	49.50	5.25	10.84



(X)



(XI)

Reaction of (VI) with Hexafluoroacetone (HFA):

A solution of (VI) (500 mg, 1 mmol) in 50 ml pentane was cooled in a Young's tube to liquid nitrogen temperature. An excess of HFA (approx. 500 ml, 10 mmol) was condensed into the tube which was sealed and allowed to warm to -30 °C. After 3 days the products were chromatographed on alumina. The main band (pale yellow) was eluted in an ether:pentane 3:1 mixture. There were traces of a red material (ether fraction) but not of sufficient quantity to allow characterisation. The yellow band yielded 300 mg, 40 % of (XI) upon recrystallisation from pentane at -30 °C.

Data for (XI): $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5\{C(CF_3)_2OH\}_2)]$.

Colour: Yellow Solubility: Hexane

N.m.r. Spectra:

^1H: (C_6D_6) 6.13 (s, 1 H, H_a), 5.57 (s, 2 H, H_c), 4.30 (s, 2 H, OH), 3.23 (t (virtual) 18 H, $\{P(OCH_3)_3\}_2$ $^3J_{P-H}$ = 10.7 Hz), 2.33 (t, 2 H, CH_2Bu^t, $^4J_{P-H}$ = 4.7 Hz), 1.07 (s, 9 H, $C(CH_3)_3$).

$^{13}C\text{-}\{^1H\}$: (C_6D_6) 311.6 (t, Mo≡C, $^2J_{P-C}$ = 38.5 Hz), 100.1 (s, C_b), 96.7 (s, C_a), 91.3 (s, C_c), 76. (m (septet), C_d, $^2J_{C-F}$ = 29.4 Hz), 64.2 (s, CH_2Bu^t), 51.2 (s, $\{P(OCH_3)_3\}_2$) 32.5 (s, $C(CH_3)_3$), 29.4 (s, $c(CH_3)_3$).

$^{31}P\text{-}\{^1H\}$: (C_6D_6) 197.8, s.

$^{19}F-\{^{1}H\}$: (C_6D_6) 221, multiplet, shift relative to $CFCl_3$.

Mass Spectrum: m/e = 824 (M^+).

Analysis:

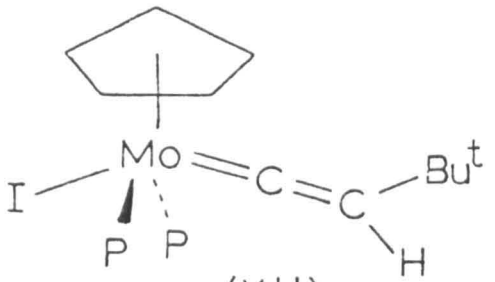
	C	H
Calc. %	33.50	4.13
Found %	33.55	4.28

Reaction of (VI) with Perfluoroalkyliodides (CD_3I and C_3F_7I).

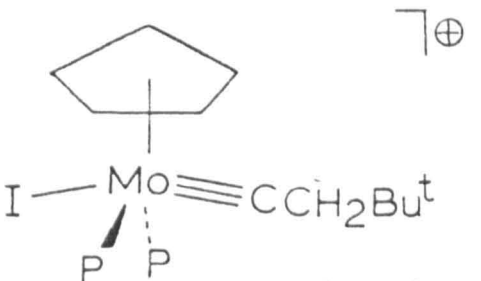
The method of Baker et al[8] was followed; 2 g of (VI) (4 mmol) was dissolved in 50 ml of hexane in a Young's tube. The vessel was cooled by liquid nitrogen and an approximate 10 fold excess of either CF_3I or C_3F_7I was condensed into it. The reaction was then allowed to proceed at -30 °C for three days. Typically, large yellow-brown crystalline needles appeared on the sides of the tube. These could be isolated by filtration and washing with ether. The soluble products the red vinylidene (XII) and the green carbene complex [Mo=C(CH_2Bu^t)PO(OMe)$_2$-{P(OMe)$_3$}(η-C_5H_5)I] could be separated by cold column chromatography on alumina, (XII) eluting first in a 2:1 hexane:ether mixture.

The yields of (XII) and the carbene species varied with the reaction. Use of C_3F_7I appeared to increase the yield of (XII) to 1.35 g (55 %) at the expense of the carbene (0.3 g, 12 %). The reaction with CF_3I gave roughly equal amounts of (XII) and the carbene.

The yield of the carbene was also reduced if the reaction was terminated after only 1 or 2 days. The yellow-brown crystals, found to contain the cation of (XIII), were converted to the green carbene upon dissolution in 20 ml THF, conversion being complete after several hours at room temperature. Maximum yield of the yellow-brown material was 0.4 g.



(XII)



(XIII)

Data for $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I][X]$.

X = F, $CF_3(C_3F_7)$?

Colour: Pale yellow-brown Solubility: CH_2Cl_2

N.m.r. Spectra:

^1H: ($CDCl_3$) 5.82 (s, 5 H, $C_5\underline{H}_5$) 3.71 (t, virtual 18 H, $\{P(O\underline{CH}_3)_3\}_2$, J_{P-H} 0 11.2 Hz), 2.60 (t, 2 H, $C\underline{H}_2Bu^t$, $^4J_{P-H}$ = 7.4 Hz), 0.84 (s, 9 H, $C(\underline{CH}_3)_3$).

$^{13}C\text{-}\{^1H\}$: (CD_2Cl_2) 392.1 (t, Mo≡C, $^2J_{P-C}$ = 31.5 Hz), 100.6 (s, $\underline{C}_5H_5$), 70.0 (s, $\underline{CH}_2Bu^t$), 60.0 (s, $\{P(O\underline{CH}_3)_3\}_2$) 35.1 (s, $\underline{C}(CH_3)_3$), 30.0 (s, $C(CH_3)_3$)

$^{31}P\text{-}\{^1H\}$: (CD_2Cl_2) 126.4, s.

Reaction of (XII) with [HBF_4].

To a stirred solution of (XII) (200 mg, 0.3 mmol) in 20 ml Et_2O at -78 °C was added dropwise [$HBF_4.Et_2O$] complex. A pale yellow precipatate was formed. The end point of the reaction was reached when no red colour persisted in solution. The product (XIII) was filtered, washed with 2 x 20 ml of Et_2O and recrystallised from CH_2Cl_2/Et_2O to give 179 mg (85 % yield) of pale-yellow microcrystals.

Data for (XIII): $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I][BF_4]$.

Colour: Pale yellow Solubility: CH_2Cl_2, THF

N.m.r. Spectra:

^1H: (100 MHz - Varian Associates Spectrometer) (CD_2Cl_2) 5.89 (t, 5 H, $C_5\underline{H}_5$, $^3J_{P-H}$ = 1 Hz), 3.83 (t (virtual), 18 H, $\{P(OC\underline{H}_3)_3\}_2$, J_{P-H} = 12 Hz), 2.74 (t, 2 H, $C\underline{H}_2Bu^t$, $^4J_{P-H}$ = 7.5 Hz), 1.03 (s, $C(C\underline{H}_3)_3$).

$^{13}C\text{-}\{^1H\}$: (90 MHz) 392.6 (t, Mo≡$\underline{C}$, $^2J_{P-C}$ = 33 Hz), 101.0 (s, $\underline{C}_5H_5$), 70.4 (s, $\underline{C}H_2$), 56.9 (s, $\{P(O\underline{C}H_3)_3\}_2$, 35.0 (s, $\underline{C}(CH_3)_3$), 30.1 (s, $C(\underline{C}H_3)_3$).

$^{31}P\text{-}\{^1H\}$: 124.6, s.

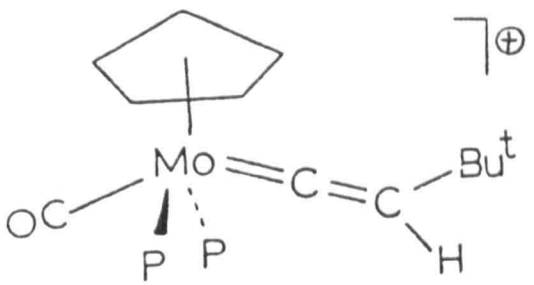
Analysis:

	C	H
Calc. %	28.90	4.82
Found %	29.98	5.18

Reaction of (IV) with [HBF_4].

[$HBF_4.Et_2O$] complex was added dropwise to an ether solution of (IV) (260 mg, 0.5 mmol in 20 ml) until all colour had disappeared from solution, leaving a pale yellow precipitate. This was filtered, washed with Et_2O (2 x 20 ml) and recrystallised from CH_2Cl_2/Et_2O to give 290 mg (90 %) of compound (XV). Crystals of (XV) were found to be unstable at room temperature, rearranging over a period of days to the acetylene complex (I) with loss of carbon monoxide. The compound was indefinitely stable in CH_2Cl_2 solution in the presence of a 10 fold excess of acid (HBF_4) under a nitrogen atmosphere.

The complex (XV) could be reversibly deprotonated back to the acetylide complex (IV). 100 mg (o.15 mmol) of (XV) were dissolved in 20 ml THF and 1 ml (7 mmol) of NEt_3 (ρ = 0.72 g cm^{-3} was added. The solution was stirred for one hour at room temperature, volatiles were removed, yielding a yellow solid. This was left under vacuum for 1 day and recrystallised from hexane giving 80 mg (90 %) of (IV).



(XV)

Data for (XV): $[Mo(CO)(C{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)I][BF_4]$.

Colour: Pale yellow Solubility: CH_2Cl_2

N.m.r. Spectra: (-80 °C).

^1H: (CD_2Cl_2) (90 MHz) 6.13 (t, 5 H, $C_5\underline{H}_5$, $^3J_{P-H}$ = 2 Hz), 5.30 (t, H, $C\underline{H}Bu^t$, $^4J_{P-H}$ = 0.8 Hz), 3.88 (t (virtual), 18 H, $\{P(OCH_3)_3\}_2$, J_{P-H} = 11.4 Hz), 1.05 (s, $C(C\underline{H}_3)_3$).

$^{13}C-\{^1H\}$: (CD_2Cl_2) 338.6 (t, $\underline{C}{=}CHBu^t$, $^2J_{P-C}$ = 61 Hz), 228.7 (t, $\underline{C}O$, $^2J_{P-C}$ = 28 Hz), 135.0 (t, $C{=}\underline{C}HBu^t$, $^3J_{P-C}$ = 15 Hz), 92.5 (s, $\underline{C}_5H_5$), 55.8 (s, $\{P(O\underline{C}H_3)_3\}_2$), 34.8 (s, $\underline{C}(CH_3)_3$), 30.0 (s, $C(\underline{C}H_3)_3$).

$^{31}P-\{^1H\}$: (CD_2Cl_2) 136.3, s.

No reliable analysis could be obtained due to the unstability of the compound in the solid state.

References for Section 3

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Tables for Section 1

(I)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	6999(1)	4310(1)	850(1)	36(1)*
P(1)	8356(1)	3861(1)	992(1)	45(1)*
P(2)	7307(1)	4807(1)	-401(1)	43(1)*
F(1)	4913(5)	7827(5)	2191(5)	172(5)*
F(2)	4709(7)	8244(8)	1069(5)	287(8)*
F(3)	8756(5)	1754(7)	3205(8)	308(8)*
F(4)	4620(10)	8948(6)	1961(6)	284(9)*
O(1)	8725(3)	3808(3)	1836(3)	61(2)*
O(2)	8471(4)	3014(3)	657(3)	65(2)*
O(3)	9050(3)	4369(3)	618(3)	59(2)*
O(4)	8040(3)	5387(3)	-505(3)	57(2)*
O(5)	6531(3)	5223(3)	-751(3)	59(2)*
O(6)	7519(3)	4229(3)	-1062(3)	64(2)*
B	4509(7)	8276(6)	1741(8)	85(5)*
C(1)	8301(6)	3371(6)	2403(5)	86(5)*
C(2)	9240(7)	2609(7)	694(7)	104(5)*
C(3)	9874(6)	4460(8)	883(8)	117(6)*
C(4)	8120(7)	6081(5)	-99(6)	93(5)*
C(5)	6534(6)	5529(7)	-1518(5)	92(5)*
C(6)	8304(6)	3870(6)	-1157(5)	83(4)*
C(7)	7564(4)	5132(4)	1450(4)	45(3)*
C(8)	6789(4)	5306(4)	1393(4)	38(2)*
C(9)	6232(5)	5923(4)	1673(5)	52(3)*
C(10)	5362(7)	5666(8)	1712(10)	206(11)*
C(11)	6470(9)	6191(10)	2434(8)	202(9)*
C(12)	6223(12)	6534(7)	1103(11)	252(12)*
C(13)	6611(6)	3122(5)	342(6)	74(4)*
C(14)	6488(6)	3131(5)	1129(5)	84(4)*
C(15)	5867(6)	3660(5)	1291(5)	77(4)*
C(16)	5615(5)	3980(5)	592(5)	66(3)*
C(17)	6072(5)	3630(5)	22(5)	69(4)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

(I)

Table 2. Bond lengths (Å)

Mo-P(1)	2.367(2)	Mo-P(2)	2.414(2)
Mo-C(7)	2.006(7)	Mo-C(8)	2.014(7)
Mo-C(13)	2.347(8)	Mo-C(14)	2.276(9)
Mo-C(15)	2.306(9)	Mo-C(16)	2.379(9)
Mo-C(17)	2.412(9)	P(1)-O(1)	1.601(5)
P(1)-O(2)	1.603(6)	P(1)-O(3)	1.583(6)
P(2)-O(4)	1.579(6)	P(2)-O(5)	1.586(6)
P(2)-O(6)	1.576(6)	F(1)-B	1.293(15)
F(2)-B	1.226(16)	F(3)-Ba	1.236(14)
F(4)-B	1.248(15)	O(1)-C(1)	1.431(11)
O(2)-C(2)	1.444(12)	O(3)-C(3)	1.434(11)
O(4)-C(4)	1.412(11)	O(5)-C(5)	1.449(11)
O(6)-C(6)	1.438(11)	B-F(3a)	1.236(14)
C(7)-H(7)	0.913(57)	C(7)-C(8)	1.307(10)
C(8)-C(9)	1.495(10)	C(9)-C(10)	1.493(13)
C(9)-C(11)	1.467(17)	C(9)-C(12)	1.463(18)
C(13)-C(14)	1.396(14)	C(13)-C(17)	1.371(12)
C(14)-C(15)	1.403(13)	C(15)-C(16)	1.410(13)
C(16)-C(17)	1.389(12)		

(I)

Table 3. Bond angles (°)

P(1)-Mo-P(2)	91.1(1)	P(1)-Mo-C(7)	75.5(2)
P(2)-Mo-C(7)	97.1(2)	P(1)-Mo-C(8)	113.3(2)
P(2)-Mo-C(8)	98.9(2)	C(7)-Mo-C(8)	37.9(3)
P(1)-Mo-C(13)	90.0(2)	P(2)-Mo-C(13)	91.7(2)
C(7)-Mo-C(13)	163.2(3)	C(8)-Mo-C(13)	153.9(3)
P(1)-Mo-C(14)	91.2(3)	P(2)-Mo-C(14)	126.8(2)
C(7)-Mo-C(14)	134.7(3)	C(8)-Mo-C(14)	128.1(3)
C(13)-Mo-C(14)	35.1(3)	P(1)-Mo-C(15)	123.7(2)
P(2)-Mo-C(15)	130.6(2)	C(7)-Mo-C(15)	123.1(3)
C(8)-Mo-C(15)	97.4(3)	C(13)-Mo-C(15)	58.3(3)
C(14)-Mo-C(15)	35.7(3)	P(1)-Mo-C(16)	146.3(2)
P(2)-Mo-C(16)	96.5(2)	C(7)-Mo-C(16)	135.3(3)
C(8)-Mo-C(16)	97.9(3)	C(13)-Mo-C(16)	57.0(3)
C(14)-Mo-C(16)	58.2(3)	C(15)-Mo-C(16)	35.0(3)
P(1)-Mo-C(17)	119.3(2)	P(2)-Mo-C(17)	76.2(2)
C(7)-Mo-C(17)	163.3(3)	C(8)-Mo-C(17)	127.1(3)
C(13)-Mo-C(17)	33.5(3)	C(14)-Mo-C(17)	56.9(3)
C(15)-Mo-C(17)	57.0(3)	C(16)-Mo-C(17)	33.7(3)
Mo-P(1)-O(1)	118.0(2)	Mo-P(1)-O(2)	112.1(2)
O(1)-P(1)-O(2)	104.0(3)	Mo-P(1)-O(3)	116.2(2)
O(1)-P(1)-O(3)	98.4(3)	O(2)-P(1)-O(3)	106.4(3)
Mo-P(2)-O(4)	119.6(2)	Mo-P(2)-O(5)	110.4(2)
O(4)-P(2)-O(5)	105.6(3)	Mo-P(2)-O(6)	118.9(2)
O(4)-P(2)-O(6)	99.2(3)	O(5)-P(2)-O(6)	100.7(3)
P(1)-O(1)-C(1)	119.4(5)	P(1)-O(2)-C(2)	122.5(6)
P(1)-O(3)-C(3)	127.0(6)	P(2)-O(4)-C(4)	124.3(6)
P(2)-O(5)-C(5)	121.7(5)	P(2)-O(6)-C(6)	124.2(5)
F(1)-B-F(2)	115.1(12)	F(1)-B-F(4)	108.0(12)
F(2)-B-F(4)	107.5(13)	F(1)-B-F(3a)	115.8(12)
F(2)-B-F(3a)	109.6(13)	F(4)-B-F(3a)	99.2(13)
Mo-C(7)-H(7)	153.9(39)	Mo-C(7)-C(8)	71.4(4)
H(7)-C(7)-C(8)	133.8(37)	Mo-C(8)-C(7)	70.7(4)
Mo-C(8)-C(9)	152.0(5)	C(7)-C(8)-C(9)	137.2(7)
C(8)-C(9)-C(10)	112.2(8)	C(8)-C(9)-C(11)	111.6(8)
C(8)-C(9)-C(12)	107.9(9)	C(9)-H(10a)-C(10)	76.2(7)
Mo-C(13)-C(14)	69.7(5)	Mo-C(13)-C(17)	75.9(5)
C(14)-C(13)-C(17)	107.7(8)	Mo-C(14)-C(13)	75.2(5)
Mo-C(14)-C(15)	73.3(5)	C(13)-C(14)-C(15)	108.2(8)
Mo-C(15)-C(14)	71.0(5)	Mo-C(15)-C(16)	75.3(5)
C(14)-C(15)-C(16)	107.2(8)	Mo-C(16)-C(15)	69.7(5)
Mo-C(16)-C(17)	74.5(5)	C(15)-C(16)-C(17)	107.2(8)
Mo-C(17)-C(13)	70.7(5)	Mo-C(17)-C(16)	71.8(5)
C(13)-C(17)-C(16)	109.7(8)		

(I)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	35(1)	36(1)	37(1)	1(1)	-1(1)	-0(1)
P(1)	46(1)	48(1)	40(1)	-1(1)	-4(1)	12(1)
P(2)	38(1)	53(1)	37(1)	3(1)	1(1)	1(1)
F(1)	153(7)	179(8)	185(8)	12(6)	-62(6)	72(6)
F(2)	265(13)	496(20)	99(7)	-102(9)	-23(7)	176(14)
F(3)	74(6)	349(14)	502(20)	305(15)	-2(9)	6(7)
F(4)	512(24)	134(8)	207(11)	-24(8)	44(13)	74(12)
O(1)	57(4)	80(4)	45(3)	5(3)	-3(3)	22(3)
O(2)	72(4)	55(3)	69(4)	-11(3)	-6(3)	26(3)
O(3)	39(3)	77(4)	60(3)	11(3)	-4(2)	1(3)
O(4)	55(3)	59(3)	58(3)	4(3)	8(3)	-5(3)
O(5)	47(3)	86(4)	45(3)	17(3)	1(3)	17(3)
O(6)	60(4)	84(4)	47(3)	-18(3)	3(3)	12(4)
B	75(8)	59(7)	120(11)	-1(8)	16(8)	18(6)
C(1)	94(8)	112(9)	51(6)	12(6)	4(6)	17(7)
C(2)	95(8)	102(8)	116(9)	-41(7)	-23(7)	63(7)
C(3)	48(6)	174(13)	130(10)	31(10)	-12(7)	-15(8)
C(4)	107(9)	67(6)	104(8)	-8(6)	51(7)	-30(7)
C(5)	72(7)	146(11)	57(6)	47(7)	0(5)	18(7)
C(6)	85(8)	99(8)	64(6)	-17(6)	-3(6)	31(6)
C(7)	43(5)	44(4)	48(5)	-6(4)	-6(4)	-0(4)
C(8)	38(5)	45(4)	30(4)	-1(3)	-3(3)	6(3)
C(9)	38(5)	58(5)	59(5)	-10(4)	1(4)	11(4)
C(10)	52(8)	163(13)	402(28)	-167(16)	-11(12)	40(9)
C(11)	185(15)	294(21)	128(12)	-145(14)	-86(11)	172(15)
C(12)	354(25)	135(13)	268(21)	105(13)	229(19)	184(16)
C(13)	74(6)	41(5)	107(7)	-22(5)	-9(6)	-12(5)
C(14)	104(8)	55(6)	93(7)	27(5)	-23(6)	-37(6)
C(15)	74(7)	84(7)	74(7)	-1(6)	20(5)	-37(6)
C(16)	50(5)	66(6)	82(7)	-9(5)	-5(5)	-14(5)
C(17)	65(6)	66(6)	76(6)	-11(5)	-9(5)	-29(5)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

(I)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
H(1a)	8630	3400	2855	101
H(1b)	8284	2851	2227	101
H(1c)	7757	3542	2515	101
H(2a)	9091	2098	551	117
H(2b)	9472	2605	1196	117
H(2c)	9634	2806	338	117
H(3a)	10212	4393	441	121
H(3b)	10061	4127	1282	121
H(3c)	9906	4982	1051	121
H(4a)	8638	6331	-161	106
H(4b)	7977	6070	431	106
H(4c)	7709	6355	-379	106
H(5a)	5981	5608	-1686	102
H(5b)	6824	5235	-1892	102
H(5c)	6797	6016	-1452	102
H(6a)	8241	3569	-1611	95
H(6b)	8497	3550	-750	95
H(6c)	8691	4272	-1248	95
H(7)	8013(36)	5385(32)	1628(33)	34(17)
H(10a)	5679	5559	2160	189
H(10b)	5092	5207	1547	189
H(10c)	4961	6050	1827	189
H(11a)	6795	5849	2736	196
H(11b)	6101	6467	2759	196
H(11c)	6822	6547	2175	196
H(12a)	5772	6880	1159	234
H(12b)	6321	6442	571	234
H(12c)	6703	6754	1330	234
H(13)	6996	2809	71	88
H(14)	6786	2831	1494	97
H(15)	5651	3777	1787	94
H(16)	5209	4370	521	80
H(17)	6022	3729	-514	79

(II)

Table 1. Atomic coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
Mo	2479(1)	2227(1)	3204(1)	17(1)*
P(1)	2882(1)	540(1)	3643(1)	20(1)*
P(2)	935(1)	2028(1)	3963(1)	22(1)*
P(3)	4269(1)	2568(1)	3747(1)	23(1)*
O(1)	1696(1)	-334(1)	3768(1)	26(1)*
O(2)	3533(1)	415(1)	4401(1)	27(1)*
O(3)	3680(1)	-103(1)	3110(1)	28(1)*
O(4)	-15(1)	1233(1)	3626(1)	33(1)*
O(5)	122(1)	3007(1)	4167(1)	30(1)*
O(6)	1161(1)	1627(1)	4765(1)	31(1)*
O(7)	5330(1)	1713(1)	3742(1)	34(1)*
O(8)	4516(1)	2902(1)	4562(1)	38(1)*
O(9)	4902(1)	3540(1)	3365(1)	28(1)*
C(1)	1237(2)	-700(2)	3163(1)	33(1)*
C(2)	3352(2)	-326(2)	4950(1)	40(1)*
C(3)	4150(2)	-1100(2)	3314(1)	40(1)*
C(4)	-994(2)	928(2)	4010(1)	49(1)*
C(5)	-392(2)	3625(2)	3608(1)	41(1)*
C(6)	651(3)	2005(3)	5393(1)	58(1)*
C(7)	5796(2)	1404(2)	3084(1)	42(1)*
C(8)	3652(2)	2569(2)	5132(1)	37(1)*
C(9)	5946(2)	3983(2)	3660(1)	41(1)*
C(10)	2407(1)	3712(1)	3833(1)	23(1)*
C(11)	2592(2)	4688(1)	3615(1)	26(1)*
C(12)	2466(2)	5696(1)	4032(1)	31(1)*
C(13)	1948(2)	5540(2)	4750(1)	44(1)*
C(14)	3677(2)	6169(2)	4151(1)	45(1)*
C(15)	1743(2)	6456(2)	3590(1)	51(1)*
C(16)	1194(2)	2255(2)	2199(1)	33(1)*
C(17)	1731(2)	3235(2)	2259(1)	29(1)*
C(18)	2913(2)	3092(2)	2174(1)	30(1)*
C(19)	3107(2)	2017(2)	2058(1)	36(1)*
C(20)	2043(2)	1504(2)	2074(1)	39(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-P(1)	2.352(1)	Mo-P(2)	2.367(1)
Mo-P(3)	2.359(1)	Mo-C(10)	2.243(2)
Mo-C(16)	2.370(2)	Mo-C(17)	2.340(2)
Mo-C(18)	2.307(2)	Mo-C(19)	2.323(2)
Mo-C(20)	2.356(2)	P(1)-O(1)	1.634(1)
P(1)-O(2)	1.599(1)	P(1)-O(3)	1.624(1)
P(2)-O(4)	1.619(1)	P(2)-O(5)	1.629(1)
P(2)-O(6)	1.606(1)	P(3)-O(7)	1.640(1)
P(3)-O(8)	1.606(1)	P(3)-O(9)	1.620(1)
O(1)-C(1)	1.429(2)	O(2)-C(2)	1.425(2)
O(3)-C(3)	1.437(2)	O(4)-C(4)	1.436(3)
O(5)-C(5)	1.431(3)	O(6)-C(6)	1.432(3)
O(7)-C(7)	1.430(3)	O(8)-C(8)	1.411(2)
O(9)-C(9)	1.441(2)	C(10)-C(11)	1.336(3)
C(10)-H(10)	0.958(20)	C(11)-C(12)	1.518(3)
C(11)-H(11)	1.017(23)	C(12)-C(13)	1.527(3)
C(12)-C(14)	1.531(3)	C(12)-C(15)	1.531(3)
C(16)-C(17)	1.406(3)	C(16)-C(20)	1.411(3)
C(17)-C(18)	1.414(3)	C(18)-C(19)	1.413(3)
C(19)-C(20)	1.412(3)		

Table 3. Bond angles (°)

P(1)-Mo-P(2)	80.6(1)	P(1)-Mo-P(3)	81.5(1)
P(2)-Mo-P(3)	117.1(1)	P(1)-Mo-C(10)	127.1(1)
P(2)-Mo-C(10)	74.1(1)	P(3)-Mo-C(10)	70.5(1)
P(1)-Mo-C(16)	114.0(1)	P(2)-Mo-C(16)	90.3(1)
P(3)-Mo-C(16)	151.0(1)	C(10)-Mo-C(16)	111.8(1)
P(1)-Mo-C(17)	146.8(1)	P(2)-Mo-C(17)	104.3(1)
P(3)-Mo-C(17)	122.0(1)	C(10)-Mo-C(17)	85.1(1)
C(16)-Mo-C(17)	34.7(1)	P(1)-Mo-C(18)	133.4(1)
P(2)-Mo-C(18)	139.4(1)	P(3)-Mo-C(18)	92.9(1)
C(10)-Mo-C(18)	93.0(1)	C(16)-Mo-C(18)	58.5(1)
C(17)-Mo-C(18)	35.4(1)	P(1)-Mo-C(19)	98.8(1)
P(2)-Mo-C(19)	145.9(1)	P(3)-Mo-C(19)	96.3(1)
C(10)-Mo-C(19)	127.5(1)	C(16)-Mo-C(19)	58.5(1)
C(17)-Mo-C(19)	58.7(1)	C(18)-Mo-C(19)	35.5(1)
P(1)-Mo-C(20)	89.4(1)	P(2)-Mo-C(20)	111.1(1)
P(3)-Mo-C(20)	128.5(1)	C(10)-Mo-C(20)	143.0(1)
C(16)-Mo-C(20)	34.7(1)	C(17)-Mo-C(20)	57.9(1)
C(18)-Mo-C(20)	58.5(1)	C(19)-Mo-C(20)	35.1(1)
Mo-P(1)-O(1)	123.1(1)	Mo-P(1)-O(2)	119.2(1)
O(1)-P(1)-O(2)	96.7(1)	Mo-P(1)-O(3)	111.1(1)
O(1)-P(1)-O(3)	99.9(1)	O(2)-P(1)-O(3)	103.5(1)
Mo-P(2)-O(4)	111.2(1)	Mo-P(2)-O(5)	122.0(1)
O(4)-P(2)-O(5)	100.1(1)	Mo-P(2)-O(6)	120.0(1)
O(4)-P(2)-O(6)	104.6(1)	O(5)-P(2)-O(6)	95.7(1)
Mo-P(3)-O(7)	122.1(1)	Mo-P(3)-O(8)	125.2(1)
O(7)-P(3)-O(8)	95.0(1)	Mo-P(3)-O(9)	110.9(1)
O(7)-P(3)-O(9)	99.5(1)	O(8)-P(3)-O(9)	99.2(1)
P(1)-O(1)-C(1)	116.2(1)	P(1)-O(2)-C(2)	129.4(1)
P(1)-O(3)-C(3)	120.6(1)	P(2)-O(4)-C(4)	121.7(1)
P(2)-O(5)-C(5)	119.0(1)	P(2)-O(6)-C(6)	127.5(1)
P(3)-O(7)-C(7)	120.1(1)	P(3)-O(8)-C(8)	125.1(1)
P(3)-O(9)-C(9)	121.2(1)	Mo-C(10)-C(11)	128.2(1)
Mo-C(10)-H(10)	116.6(12)	C(11)-C(10)-H(10)	113.1(12)
C(10)-C(11)-C(12)	128.1(2)	C(10)-C(11)-H(11)	121.9(14)
C(12)-C(11)-H(11)	110.0(14)	C(11)-C(12)-C(13)	113.1(2)
C(11)-C(12)-C(14)	108.5(2)	C(11)-C(12)-C(15)	108.4(2)
Mo-C(16)-C(17)	71.5(1)	Mo-C(16)-C(20)	72.1(1)
C(17)-C(16)-C(20)	107.7(2)	Mo-C(17)-C(16)	73.8(1)
Mo-C(17)-C(18)	71.0(1)	C(16)-C(17)-C(18)	106.3(2)
Mo-C(18)-C(17)	73.6(1)	Mo-C(18)-C(19)	72.6(1)
C(17)-C(18)-C(19)	107.9(2)	Mo-C(19)-C(18)	71.6(1)
Mo-C(19)-C(20)	73.7(1)	C(18)-C(19)-C(20)	107.5(2)
Mo-C(20)-C(16)	73.1(1)	Mo-C(20)-C(19)	71.1(1)
C(16)-C(20)-C(19)	108.5(2)		

Table 4. Anisotropic thermal parameters ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	16(1)	23(1)	13(1)	1(1)	-0(1)	-0(1)
P(1)	19(1)	23(1)	18(1)	1(1)	1(1)	-1(1)
P(2)	19(1)	29(1)	18(1)	2(1)	2(1)	1(1)
P(3)	18(1)	32(1)	19(1)	4(1)	-2(1)	-3(1)
O(1)	25(1)	27(1)	26(1)	1(1)	-0(1)	-7(1)
O(2)	27(1)	31(1)	22(1)	6(1)	-4(1)	-4(1)
O(3)	31(1)	27(1)	27(1)	2(1)	8(1)	6(1)
O(4)	21(1)	43(1)	35(1)	-4(1)	4(1)	-7(1)
O(5)	27(1)	36(1)	28(1)	3(1)	7(1)	11(1)
O(6)	33(1)	42(1)	19(1)	6(1)	6(1)	9(1)
O(7)	21(1)	44(1)	37(1)	13(1)	1(1)	3(1)
O(8)	30(1)	63(1)	21(1)	1(1)	-5(1)	-17(1)
O(9)	22(1)	35(1)	27(1)	5(1)	-1(1)	-8(1)
C(1)	32(1)	33(1)	34(1)	-4(1)	-4(1)	-9(1)
C(2)	44(1)	47(1)	29(1)	17(1)	-3(1)	-9(1)
C(3)	46(1)	32(1)	43(1)	4(1)	12(1)	14(1)
C(4)	31(1)	59(1)	59(1)	-3(1)	16(1)	-14(1)
C(5)	34(1)	49(1)	41(1)	14(1)	6(1)	16(1)
C(6)	71(2)	82(2)	22(1)	5(1)	15(1)	27(2)
C(7)	26(1)	45(1)	54(1)	7(1)	10(1)	4(1)
C(8)	40(1)	49(1)	21(1)	3(1)	-3(1)	-9(1)
C(9)	29(1)	52(1)	42(1)	5(1)	-5(1)	-16(1)
C(10)	22(1)	27(1)	20(1)	-2(1)	-1(1)	1(1)
C(11)	30(1)	29(1)	24(1)	-1(1)	1(1)	-2(1)
C(12)	34(1)	27(1)	33(1)	-2(1)	-0(1)	2(1)
C(13)	53(1)	39(1)	40(1)	-10(1)	8(1)	2(1)
C(14)	45(1)	37(1)	51(1)	-7(1)	-3(1)	-8(1)
C(15)	56(1)	36(1)	56(1)	6(1)	-4(1)	15(1)
C(16)	30(1)	52(1)	17(1)	5(1)	-8(1)	-10(1)
C(17)	32(1)	36(1)	17(1)	5(1)	-6(1)	5(1)
C(18)	30(1)	42(1)	18(1)	10(1)	1(1)	-6(1)
C(19)	36(1)	53(1)	17(1)	1(1)	4(1)	14(1)
C(20)	62(1)	35(1)	16(1)	-2(1)	-5(1)	-2(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	681	-1184	3328	49(7)
H(1b)	1735	-1053	2850	47(7)
H(1c)	656	-138	2912	39(6)
H(2a)	4079	-404	5197	69(9)
H(2b)	3113	-988	4756	115(13)
H(2c)	2801	-83	5274	92(11)
H(3a)	4466	-1419	2911	44(6)
H(3b)	3570	-1551	3468	59(8)
H(3c)	4728	-989	3682	61(8)
H(4a)	-1451	511	3664	57(6)
H(4b)	-1433	1514	4162	56(6)
H(4c)	-763	513	4415	70(9)
H(5a)	-672	4112	3844	54(7)
H(5b)	-651	3202	3267	64(8)
H(5c)	161	4001	3346	66(6)
H(6a)	1105	1774	5799	77(9)
H(6b)	-101	1713	5411	106(13)
H(6c)	602	2754	5397	90(11)
H(7a)	6347	866	3197	63(6)
H(7b)	6166	1979	2860	68(9)
H(7c)	5211	1127	2765	59(6)
H(8a)	3749	3205	5413	51(7)
H(8b)	4299	2089	5403	59(8)
H(8c)	3122	2292	5003	45(7)
H(9a)	6267	4401	3302	63(6)
H(9b)	6443	3411	3787	53(7)
H(9c)	5826	4404	4072	66(9)
H(13a)	1905	6207	4980	64(8)
H(13b)	2385	5067	5048	45(7)
H(13c)	1193	5267	4665	49(7)
H(14a)	3602	6824	4393	56(6)
H(14b)	4020	6284	3703	47(7)
H(14c)	4149	5706	4436	63(8)
H(15a)	1729	7104	3849	71(9)
H(15b)	979	6195	3522	47(7)
H(15c)	2062	6575	3135	56(8)
H(16)	394	2122	2236	37(6)
H(17)	1359	3889	2342	34(6)
H(18)	3484	3631	2193	51(7)
H(19)	3831	1694	1962	62(8)
H(20)	1918	768	2010	64(8)
H(10)	2177(17)	3676(15)	4315(10)	29(5)
H(11)	2861(20)	4845(19)	3119(12)	46(6)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	7004(1)	-1019(1)	7129(1)	14(1)*
P(1)	7237(1)	1127(1)	8579(1)	19(1)*
P(2)	8787(1)	-2453(1)	6688(1)	31(1)*
O(1)	5475(3)	688(3)	8873(2)	23(1)*
O(2)	7805(3)	3042(3)	8717(2)	26(1)*
O(3)	8374(3)	1395(3)	9494(2)	29(1)*
O(4)	7779(3)	-4387(3)	6298(2)	32(1)*
O(5a)	9217(6)	-2691(5)	5607(3)	24(2)*
O(5b)	10396(7)	-1892(7)	6303(4)	25(2)
O(6a)	10533(5)	-1983(5)	7176(3)	26(2)*
O(6b)	9824(7)	-2641(6)	7587(3)	21(2)
O(7)	6704(3)	-2796(3)	8490(2)	29(1)*
C(1)	5254(6)	1739(5)	9745(2)	31(2)*
C(2)	7581(5)	3544(5)	7971(3)	27(2)*
C(3)	10069(5)	2499(6)	9800(3)	40(2)*
C(4)	8496(6)	-5572(5)	5888(3)	33(2)*
C(5)	10331(6)	-1328(5)	5512(3)	36(2)*
C(6)	11002(6)	-1250(5)	8227(3)	39(2)*
C(7)	6850(5)	-2105(4)	7983(2)	19(2)*
C(8)	9407(5)	945(4)	7372(2)	19(2)*
C(9)	10712(5)	2088(4)	7495(2)	20(2)*
C(10)	12332(5)	3499(4)	7709(2)	20(2)*
C(11)	12090(5)	5149(4)	8034(3)	28(2)*
C(12)	13533(5)	3541(5)	8471(3)	28(2)*
C(13)	13106(5)	3333(5)	6842(3)	30(2)*
C(14)	5781(5)	-519(5)	5923(3)	32(2)*
C(15)	5841(5)	-2099(5)	5553(2)	29(2)*
C(16)	4845(5)	-3104(5)	5970(2)	26(2)*
C(17)	4158(5)	-2138(5)	6599(3)	27(2)*
C(18)	4737(5)	-553(5)	6574(3)	31(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-P(1)	2.409(1)	Mo-P(2)	2.394(1)
Mo-C(7)	1.931(4)	Mo-C(8)	2.168(3)
Mo-C(14)	2.396(5)	Mo-C(15)	2.347(4)
Mo-C(16)	2.306(3)	Mo-C(17)	2.327(4)
Mo-C(18)	2.375(5)	P(1)-O(1)	1.601(3)
P(1)-O(2)	1.610(3)	P(1)-O(3)	1.601(3)
P(2)-O(4)	1.575(3)	P(2)-O(5a)	1.723(5)
P(2)-O(5b)	1.565(6)	P(2)-O(6a)	1.522(5)
P(2)-O(6b)	1.737(6)	O(1)-C(1)	1.461(5)
O(2)-C(2)	1.436(6)	O(3)-C(3)	1.423(4)
O(4)-C(4)	1.447(6)	O(5a)-O(5b)	1.268(6)
O(5a)-C(5)	1.370(6)	O(5b)-O(6a)	1.408(8)
O(5b)-C(5)	1.518(8)	O(6a)-O(6b)	1.113(8)
O(6a)-C(6)	1.527(5)	O(6b)-C(6)	1.349(5)
O(7)-C(7)	1.174(5)	C(8)-C(9)	1.213(5)
C(9)-C(10)	1.487(5)	C(10)-C(11)	1.545(6)
C(10)-C(12)	1.538(6)	C(10)-C(13)	1.546(6)
C(14)-C(15)	1.412(7)	C(14)-C(18)	1.419(6)
C(15)-C(16)	1.412(6)	C(16)-C(17)	1.416(6)
C(17)-C(18)	1.403(6)		

Table 3. Bond angles (°)

P(1)-Mo-P(2)	129.1(1)	P(1)-Mo-C(7)	76.9(1)
P(2)-Mo-C(7)	78.0(1)	P(1)-Mo-C(8)	74.6(1)
P(2)-Mo-C(8)	76.0(1)	C(7)-Mo-C(8)	113.4(2)
P(1)-Mo-C(14)	108.2(1)	P(2)-Mo-C(14)	114.9(1)
C(7)-Mo-C(14)	151.6(1)	C(8)-Mo-C(14)	94.7(2)
P(1)-Mo-C(15)	142.0(1)	P(2)-Mo-C(15)	86.6(1)
C(7)-Mo-C(15)	130.4(1)	C(8)-Mo-C(15)	107.7(1)
C(14)-Mo-C(15)	34.6(2)	P(1)-Mo-C(16)	135.2(1)
P(2)-Mo-C(16)	91.6(1)	C(7)-Mo-C(16)	97.8(1)
C(8)-Mo-C(16)	142.5(1)	C(14)-Mo-C(16)	58.3(1)
C(15)-Mo-C(16)	35.3(1)	P(1)-Mo-C(17)	99.7(1)
P(2)-Mo-C(17)	125.5(1)	C(7)-Mo-C(17)	93.8(2)
C(8)-Mo-C(17)	149.5(2)	C(14)-Mo-C(17)	57.9(2)
C(15)-Mo-C(17)	58.4(1)	C(16)-Mo-C(17)	35.6(1)
P(1)-Mo-C(18)	86.3(1)	P(2)-Mo-C(18)	144.2(1)
C(7)-Mo-C(18)	121.7(2)	C(8)-Mo-C(18)	114.9(2)
C(14)-Mo-C(18)	34.6(2)	C(15)-Mo-C(18)	57.8(2)
C(16)-Mo-C(18)	58.4(2)	C(17)-Mo-C(18)	34.7(2)
Mo-P(1)-O(1)	108.8(1)	Mo-P(1)-O(2)	122.6(1)
O(1)-P(1)-O(2)	103.6(2)	Mo-P(1)-O(3)	120.3(1)
O(1)-P(1)-O(3)	100.1(2)	O(2)-P(1)-O(3)	98.2(1)
Mo-P(2)-O(4)	110.8(1)	Mo-P(2)-O(5a)	114.5(2)
O(4)-P(2)-O(5a)	87.7(2)	Mo-P(2)-O(5b)	127.7(3)
O(4)-P(2)-O(5b)	114.4(2)	O(5a)-P(2)-O(5b)	45.1(2)
Mo-P(2)-O(6a)	127.8(2)	O(4)-P(2)-O(6a)	111.0(2)
O(5a)-P(2)-O(6a)	96.9(2)	O(5b)-P(2)-O(6a)	54.3(3)
Mo-P(2)-O(6b)	114.8(2)	O(4)-P(2)-O(6b)	87.8(2)
O(5a)-P(2)-O(6b)	128.7(3)	O(5b)-P(2)-O(6b)	92.2(3)
O(6a)-P(2)-O(6b)	39.2(3)	P(1)-O(1)-C(1)	121.1(2)
P(1)-O(2)-C(2)	122.7(2)	P(1)-O(3)-C(3)	123.5(3)
P(2)-O(4)-C(4)	123.2(2)	P(2)-O(5a)-O(5b)	60.9(3)
P(2)-O(5a)-C(5)	117.3(3)	O(5b)-O(5a)-C(5)	70.1(4)
P(2)-O(5b)-O(5a)	74.1(3)	P(2)-O(5b)-O(6a)	61.3(3)
O(5a)-O(5b)-O(6a)	130.7(5)	P(2)-O(5b)-C(5)	118.4(5)
O(5a)-O(5b)-C(5)	58.1(4)	O(6a)-O(5b)-C(5)	165.0(5)
P(2)-O(6a)-O(5b)	64.4(3)	P(2)-O(6a)-O(6b)	80.9(4)
O(5b)-O(6a)-O(6b)	141.6(4)	P(2)-O(6a)-C(6)	120.7(4)
O(5b)-O(6a)-C(6)	154.3(4)	O(6b)-O(6a)-C(6)	59.0(3)
P(2)-O(6b)-O(6a)	59.9(4)	P(2)-O(6b)-C(6)	117.8(5)
O(6a)-O(6b)-C(6)	76.0(4)	O(5a)-C(5)-O(5b)	51.8(3)
O(6a)-C(6)-O(6b)	45.0(3)	O(6b)-H(6a)-C(6)	64.0(3)
Mo-C(7)-O(7)	177.8(3)	Mo-C(8)-C(9)	176.7(4)
C(8)-C(9)-C(10)	176.2(4)	C(9)-C(10)-C(11)	109.7(4)
C(9)-C(10)-C(12)	110.3(4)	C(9)-C(10)-C(13)	110.5(3)
Mo-C(14)-C(15)	70.8(3)	Mo-C(14)-C(18)	71.9(3)
C(15)-C(14)-C(18)	107.4(4)	Mo-C(15)-C(14)	74.6(2)
Mo-C(15)-C(16)	70.8(2)	C(14)-C(15)-C(16)	108.5(4)
Mo-C(16)-C(15)	73.9(2)	Mo-C(16)-C(17)	73.0(2)
C(15)-C(16)-C(17)	107.6(4)	Mo-C(17)-C(16)	71.4(2)
Mo-C(17)-C(18)	74.5(2)	C(16)-C(17)-C(18)	108.2(4)
Mo-C(18)-C(14)	73.5(3)	Mo-C(18)-C(17)	70.8(3)
C(14)-C(18)-C(17)	108.3(4)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	16(1)	14(1)	14(1)	5(1)	4(1)	7(1)
P(1)	21(1)	17(1)	16(1)	6(1)	2(1)	6(1)
P(2)	23(1)	18(1)	52(1)	11(1)	17(1)	10(1)
O(1)	21(2)	27(1)	17(1)	4(1)	7(1)	10(1)
O(2)	35(2)	19(1)	21(1)	5(1)	6(1)	10(1)
O(3)	26(2)	30(2)	21(1)	9(1)	-5(1)	3(1)
O(4)	26(2)	19(1)	43(2)	0(1)	6(1)	11(1)
O(5a)	26(3)	24(3)	22(3)	8(2)	13(2)	10(2)
O(6a)	23(3)	27(3)	26(3)	6(2)	3(2)	12(2)
O(7)	33(2)	28(1)	31(2)	19(1)	8(1)	10(1)
C(1)	42(3)	31(2)	15(2)	4(2)	8(2)	15(2)
C(2)	29(3)	24(2)	32(2)	13(2)	5(2)	14(2)
C(3)	25(3)	62(3)	25(2)	19(2)	2(2)	8(2)
C(4)	45(3)	25(2)	30(2)	4(2)	8(2)	23(2)
C(5)	40(3)	40(3)	28(2)	9(2)	7(2)	20(2)
C(6)	40(3)	41(3)	49(3)	23(2)	16(2)	25(2)
C(7)	14(2)	18(2)	21(2)	4(2)	3(2)	6(2)
C(8)	21(2)	19(2)	22(2)	9(2)	9(2)	11(2)
C(9)	22(2)	20(2)	19(2)	5(2)	6(2)	11(2)
C(10)	16(2)	21(2)	23(2)	8(2)	5(2)	6(2)
C(11)	22(3)	24(2)	36(2)	9(2)	2(2)	8(2)
C(12)	21(3)	31(2)	33(2)	15(2)	5(2)	8(2)
C(13)	25(3)	31(2)	29(2)	12(2)	10(2)	7(2)
C(14)	29(3)	32(2)	30(2)	16(2)	-11(2)	4(2)
C(15)	28(3)	38(2)	14(2)	4(2)	3(2)	12(2)
C(16)	23(3)	21(2)	23(2)	0(2)	-6(2)	5(2)
C(17)	17(3)	37(2)	25(2)	12(2)	1(2)	11(2)
C(18)	30(3)	34(2)	24(2)	1(2)	-11(2)	20(2)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(h^2 a^{*2} U_{11} + \ldots + 2hka^*b^*U_{12})$

(IV)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
H(1a)	4109	1356	9785	60
H(1b)	5637	2865	9791	60
H(1c)	5888	1685	10240	60
H(2a)	8172	4726	8205	60
H(2b)	6435	3265	7753	60
H(2c)	8034	3029	7472	60
H(3a)	10575	2188	10223	60
H(3b)	10195	3629	10101	60
H(3c)	10591	2389	9277	60
H(4a)	8205	-6406	6143	60
H(4b)	9677	-5021	6002	60
H(4c)	8067	-6083	5235	60
H(5a)	10093	-1888	4853	60
H(5b)	11506	-778	5731	60
H(5c)	9844	-526	5679	60
H(6a)	10756	-2028	8520	60
H(6b)	10588	-418	8513	60
H(6c)	12177	-735	8288	60
H(11a)	13179	5999	8172	60
H(11b)	11626	5316	8579	60
H(11c)	11402	5197	7560	60
H(12a)	14577	4455	8609	60
H(12b)	13695	2523	8278	60
H(12c)	13057	3675	9012	60
H(13a)	14172	4215	6973	60
H(13b)	12388	3330	6361	60
H(13c)	13221	2291	6647	60
H(14)	6347	411	5766	60
H(15)	6456	-2433	5095	60
H(16)	4660	-4237	5848	60
H(17)	3423	-2504	6978	60
H(18)	4468	352	6936	60

(V)

Table 1. Atomic coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
Mo	2186(1)	2727(1)	6019(1)	31(1)*
P(1)	2537(1)	3547(1)	4935(1)	41(1)*
P(2)	3538(1)	3927(1)	6586(1)	41(1)*
O(1)	3325(2)	2857(4)	4501(2)	64(1)*
O(2)	1583(2)	3509(3)	4360(2)	56(1)*
O(3)	2977(3)	4956(4)	4851(2)	69(2)*
O(4)	4504(2)	4129(3)	6215(2)	58(1)*
O(5)	4134(2)	3462(4)	7316(2)	62(1)*
O(6)	3168(3)	5335(3)	6768(2)	73(2)*
C(1)	4342(4)	2737(6)	4734(3)	72(2)*
C(2)	1610(4)	3951(7)	3669(3)	84(3)*
C(3)	2464(5)	6085(6)	5044(4)	98(3)*
C(4)	5528(3)	4293(5)	6530(3)	67(2)*
C(5)	3629(4)	2996(6)	7853(2)	67(2)*
C(6)	3746(5)	6374(6)	6982(4)	109(3)*
C(7)	4265(3)	915(5)	6326(3)	59(2)*
C(8)	3227(3)	1403(4)	6102(2)	36(1)*
C(9)	2388(3)	658(4)	5757(2)	34(1)*
C(10)	1919(3)	-305(4)	6189(2)	34(1)*
C(11)	1227(3)	-1210(4)	5900(2)	41(2)*
C(12)	792(3)	-2085(4)	6295(3)	51(2)*
C(13)	1047(4)	-2112(5)	7001(3)	54(2)*
C(14)	1748(4)	-1256(5)	7303(2)	57(2)*
C(15)	2172(4)	-361(4)	6907(2)	49(2)*
C(20)	2357(3)	234(4)	5013(2)	35(1)*
C(21)	1552(3)	504(4)	4512(2)	45(2)*
C(22)	1508(4)	55(5)	3843(2)	54(2)*
C(23)	2272(4)	-657(5)	3651(3)	61(2)*
C(24)	3079(4)	-939(5)	4132(3)	63(2)*
C(25)	3124(3)	-516(4)	4808(3)	50(2)*
C(30)	450(3)	2288(5)	5989(3)	56(2)*
C(31)	877(3)	2386(5)	6668(3)	55(2)*
C(32)	1212(4)	3620(6)	6795(3)	63(2)*
C(33)	994(4)	4304(5)	6173(3)	67(2)*
C(34)	516(3)	3468(6)	5675(3)	69(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-P(1)	2.398(1)	Mo-P(2)	2.367(1)
Mo-C(8)	1.963(4)	Mo-C(9)	2.249(4)
Mo-C(30)	2.381(4)	Mo-C(31)	2.340(5)
Mo-C(32)	2.337(6)	Mo-C(33)	2.352(5)
Mo-C(34)	2.392(5)	P(1)-O(1)	1.619(4)
P(1)-O(2)	1.595(3)	P(1)-O(3)	1.604(4)
P(2)-O(4)	1.591(4)	P(2)-O(5)	1.620(3)
P(2)-O(6)	1.611(4)	O(1)-C(1)	1.394(6)
O(2)-C(2)	1.437(6)	O(3)-C(3)	1.444(7)
O(4)-C(4)	1.447(5)	O(5)-C(5)	1.414(6)
O(6)-C(6)	1.370(7)	C(8)-C(7)	1.501(6)
C(8)-C(9)	1.463(5)	C(9)-C(10)	1.508(6)
C(9)-C(20)	1.520(6)	C(10)-C(11)	1.396(5)
C(10)-C(15)	1.406(6)	C(11)-C(12)	1.379(7)
C(12)-C(13)	1.382(7)	C(13)-C(14)	1.377(7)
C(14)-C(15)	1.388(7)	C(20)-C(21)	1.394(6)
C(20)-C(25)	1.400(6)	C(21)-C(22)	1.389(6)
C(22)-C(23)	1.366(7)	C(23)-C(24)	1.375(7)
C(24)-C(25)	1.393(7)	C(30)-C(31)	1.382(7)
C(30)-C(34)	1.385(8)	C(31)-C(32)	1.379(8)
C(32)-C(33)	1.409(8)	C(33)-C(34)	1.402(8)

Table 3. Bond angles (°)

P(1)-Mo-P(2)	89.8(1)	P(1)-Mo-C(8)	95.8(1)
P(2)-Mo-C(8)	80.6(1)	P(1)-Mo-C(9)	95.5(1)
P(2)-Mo-C(9)	120.5(1)	C(8)-Mo-C(9)	39.9(1)
P(1)-Mo-C(30)	111.0(1)	P(2)-Mo-C(30)	143.9(1)
C(8)-Mo-C(30)	123.9(2)	C(9)-Mo-C(30)	87.6(2)
P(1)-Mo-C(31)	142.2(1)	P(2)-Mo-C(31)	114.5(1)
C(8)-Mo-C(31)	115.6(2)	C(9)-Mo-C(31)	95.9(2)
C(30)-Mo-C(31)	34.0(2)	P(1)-Mo-C(32)	129.1(1)
P(2)-Mo-C(32)	87.0(1)	C(8)-Mo-C(32)	133.4(2)
C(9)-Mo-C(32)	129.1(2)	C(30)-Mo-C(32)	57.0(2)
C(31)-Mo-C(32)	34.3(2)	P(1)-Mo-C(33)	94.9(2)
P(2)-Mo-C(33)	93.8(1)	C(8)-Mo-C(33)	167.9(2)
C(9)-Mo-C(33)	144.1(2)	C(30)-Mo-C(33)	56.6(2)
C(31)-Mo-C(33)	57.0(2)	C(32)-Mo-C(33)	35.0(2)
P(1)-Mo-C(34)	85.8(1)	P(2)-Mo-C(34)	126.8(1)
C(8)-Mo-C(34)	152.6(2)	C(9)-Mo-C(34)	112.7(2)
C(30)-Mo-C(34)	33.7(2)	C(31)-Mo-C(34)	56.7(2)
C(32)-Mo-C(34)	57.5(2)	C(33)-Mo-C(34)	34.4(2)
Mo-P(1)-O(1)	122.0(1)	Mo-P(1)-O(2)	112.4(1)
O(1)-P(1)-O(2)	98.1(2)	Mo-P(1)-O(3)	122.5(1)
O(1)-P(1)-O(3)	94.5(2)	O(2)-P(1)-O(3)	103.1(2)
Mo-P(2)-O(4)	118.9(1)	Mo-P(2)-O(5)	121.2(1)
O(4)-P(2)-O(5)	96.0(2)	Mo-P(2)-O(6)	110.3(1)
O(4)-P(2)-O(6)	106.2(2)	O(5)-P(2)-O(6)	102.0(2)
P(1)-O(1)-C(1)	123.7(3)	P(1)-O(2)-C(2)	122.6(3)
P(1)-O(3)-C(3)	121.8(4)	P(2)-O(4)-C(4)	127.9(3)
P(2)-O(5)-C(5)	122.0(3)	P(2)-O(6)-C(6)	127.7(4)
O(3)-H(3c)-C(3)	71.8(3)	Mo-C(8)-C(7)	153.3(3)
Mo-C(8)-C(9)	80.6(2)	C(7)-C(8)-C(9)	126.0(4)
Mo-C(9)-C(8)	59.4(2)	Mo-C(9)-C(10)	116.0(3)
C(8)-C(9)-C(10)	116.8(3)	Mo-C(9)-C(20)	120.9(3)
C(8)-C(9)-C(20)	121.4(4)	C(10)-C(9)-C(20)	112.6(3)
C(9)-C(10)-C(11)	122.2(4)	C(9)-C(10)-C(15)	121.7(3)
C(11)-C(10)-C(15)	116.1(4)	C(10)-C(11)-C(12)	122.2(4)
C(11)-C(12)-C(13)	120.6(4)	C(12)-C(13)-C(14)	118.9(5)
C(13)-C(14)-C(15)	120.5(4)	C(10)-C(15)-C(14)	121.7(4)
C(9)-C(20)-C(21)	122.4(4)	C(9)-C(20)-C(25)	120.9(4)
C(21)-C(20)-C(25)	116.6(4)	C(20)-C(21)-C(22)	121.9(4)
C(21)-C(22)-C(23)	120.6(4)	C(22)-C(23)-C(24)	119.0(5)
C(23)-C(24)-C(25)	121.1(5)	C(20)-C(25)-C(24)	120.9(4)
Mo-C(30)-C(31)	71.3(3)	Mo-C(30)-C(34)	73.6(3)
C(31)-C(30)-C(34)	108.5(5)	Mo-C(31)-C(30)	74.6(3)
Mo-C(31)-C(32)	72.7(3)	C(30)-C(31)-C(32)	109.2(5)
Mo-C(32)-C(31)	73.0(3)	Mo-C(32)-C(33)	73.1(3)
C(31)-C(32)-C(33)	106.9(5)	Mo-C(33)-C(32)	71.9(3)
Mo-C(33)-C(34)	74.4(3)	C(32)-C(33)-C(34)	108.1(5)
Mo-C(34)-C(30)	72.7(3)	Mo-C(34)-C(33)	71.2(3)
C(30)-C(34)-C(33)	107.3(5)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	32(1)	29(1)	33(1)	-0(1)	4(1)	0(1)
P(1)	40(1)	44(1)	39(1)	7(1)	3(1)	-4(1)
P(2)	44(1)	40(1)	39(1)	-5(1)	4(1)	-5(1)
O(1)	55(2)	90(3)	51(2)	10(2)	14(2)	9(2)
O(2)	47(2)	81(2)	40(2)	15(2)	3(1)	-7(2)
O(3)	76(3)	64(2)	68(3)	13(2)	8(2)	-19(2)
O(4)	50(2)	77(2)	48(2)	-4(2)	6(2)	-23(2)
O(5)	54(2)	92(3)	38(2)	-0(2)	-3(2)	-15(2)
O(6)	76(3)	48(2)	94(3)	-25(2)	9(2)	-11(2)
C(1)	53(3)	108(5)	55(3)	-0(3)	9(3)	18(4)
C(2)	61(4)	145(6)	45(3)	35(4)	4(3)	-17(4)
C(3)	149(7)	47(4)	103(5)	6(3)	37(5)	26(4)
C(4)	47(3)	75(4)	80(4)	-10(3)	13(3)	-12(3)
C(5)	74(4)	81(4)	44(3)	7(3)	7(3)	12(3)
C(6)	79(5)	68(5)	182(8)	-45(5)	24(5)	-19(4)
C(7)	46(3)	51(3)	74(4)	-7(3)	-11(3)	7(2)
C(8)	33(2)	34(2)	39(2)	-0(2)	-0(2)	1(2)
C(9)	35(2)	30(2)	38(2)	1(2)	3(2)	5(2)
C(10)	35(2)	26(2)	41(3)	2(2)	6(2)	7(2)
C(11)	41(3)	36(2)	45(3)	1(2)	2(2)	-3(2)
C(12)	49(3)	41(3)	63(3)	3(2)	6(2)	-8(2)
C(13)	65(3)	40(3)	60(3)	13(3)	23(3)	4(3)
C(14)	82(4)	52(3)	37(3)	10(2)	9(3)	4(3)
C(15)	64(3)	36(3)	44(3)	-0(2)	-1(2)	-2(2)
C(20)	37(2)	26(2)	43(3)	-1(2)	11(2)	-7(2)
C(21)	47(3)	47(3)	40(3)	-5(2)	6(2)	-2(2)
C(22)	59(3)	61(3)	42(3)	-3(2)	3(2)	-12(3)
C(23)	73(4)	66(4)	48(3)	-12(3)	18(3)	-19(3)
C(24)	68(4)	53(3)	76(4)	-23(3)	39(3)	-2(3)
C(25)	46(3)	42(3)	63(3)	-11(2)	11(2)	-5(2)
C(30)	33(2)	63(3)	76(4)	-17(3)	16(2)	-3(2)
C(31)	49(3)	63(4)	57(3)	16(3)	23(2)	10(3)
C(32)	49(3)	81(4)	62(4)	-29(3)	15(3)	5(3)
C(33)	49(3)	37(3)	121(5)	4(3)	33(3)	13(2)
C(34)	37(3)	109(5)	61(3)	24(3)	10(2)	19(3)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(\underline{h}^2\underline{a}^{*2}\underline{U}_{11} + \ldots + 2\underline{hka}^*\underline{b}^*\underline{U}_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	4658	2169	4446	86
H(1b)	4498	2472	5205	86
H(1c)	4581	3592	4684	86
H(2a)	993	4400	3538	99
H(2b)	1635	3214	3380	99
H(2c)	2161	4506	3616	99
H(3a)	2259	6842	4785	111
H(3b)	2477	6254	5525	111
H(3c)	2000	5406	4909	111
H(4a)	5943	4547	6193	79
H(4b)	5726	3458	6703	79
H(4c)	5601	4896	6902	79
H(5a)	4158	2655	8179	81
H(5b)	3124	2355	7744	81
H(5c)	3343	3728	8047	81
H(6a)	3275	7046	7028	125
H(6b)	4303	6712	6782	125
H(6c)	3978	6021	7427	125
H(7a)	4692	1507	6600	70
H(7b)	4547	721	5914	70
H(7c)	4207	142	6583	70
H(11)	1045	-1222	5410	51
H(12)	309	-2681	6078	61
H(13)	742	-2718	7276	64
H(14)	1947	-1281	7792	67
H(15)	2648	239	7129	60
H(21)	1012	1018	4633	52
H(22)	935	247	3513	63
H(23)	2243	-959	3187	72
H(24)	3622	-1432	4000	73
H(25)	3686	-745	5139	63
H(30)	156	1530	5773	68
H(31)	934	1703	6998	65
H(32)	1529	3952	7225	79
H(33)	1147	5187	6102	76
H(34)	280	3673	5204	76

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	3615(1)	7584(1)	5998(1)	19(1)*
Mo(2)	6566(1)	2540(1)	9224(1)	18(1)*
P(1)	1983(1)	7773(1)	5083(1)	24(1)*
P(2)	2492(1)	8760(1)	6718(1)	23(1)*
P(3)	8501(1)	2568(1)	9997(1)	21(1)*
P(4)	7333(1)	1101(1)	8543(1)	21(1)*
O(1)	440(2)	8197(2)	5135(1)	33(1)*
O(2)	1474(2)	6672(2)	4606(1)	35(1)*
O(3)	2530(2)	8654(2)	4542(1)	34(1)*
O(10)	8928(2)	841(1)	8467(1)	27(1)*
O(11)	6770(2)	-103(1)	8789(1)	29(1)*
O(12)	6894(2)	1047(2)	7725(1)	32(1)*
O(4)	868(2)	8434(2)	6777(1)	31(1)*
O(5)	3059(2)	8917(2)	7521(1)	35(1)*
O(6)	2571(2)	10096(1)	6627(1)	35(1)*
O(7)	9966(2)	2355(2)	9702(1)	37(1)*
O(8)	8516(2)	1802(2)	10660(1)	38(1)*
O(9)	8993(3)	3722(2)	10409(1)	61(1)*
C(1)	-632(3)	7496(3)	5412(2)	41(1)*
C(2)	2428(4)	5842(3)	4470(2)	45(1)*
C(3)	1693(4)	8918(4)	3937(2)	60(1)*
C(4)	59(3)	9063(3)	7230(2)	41(1)*
C(5)	3167(4)	7932(3)	7911(2)	49(1)*
C(6)	2329(4)	10545(2)	5958(2)	46(1)*
C(7)	11228(3)	2382(3)	10141(2)	42(1)*
C(8)	8372(4)	621(3)	10574(2)	67(1)*
C(9)	8149(3)	4571(3)	10537(2)	47(1)*
C(10)	9846(3)	1654(2)	8169(2)	34(1)*
C(11)	6932(4)	-1114(2)	8403(2)	42(1)*
C(12)	5545(3)	1360(3)	7468(2)	41(1)*
C(13)	2521(2)	6407(2)	6228(1)	22(1)*
C(14)	1607(3)	5414(2)	6376(1)	27(1)*
C(15)	2365(3)	4434(2)	6705(1)	29(1)*
C(16)	1279(3)	3478(2)	6813(2)	44(1)*
C(17)	3416(3)	4017(2)	6232(2)	40(1)*
C(18)	3103(4)	4815(3)	7388(2)	47(1)*
C(19)	5568(3)	8772(2)	5672(2)	34(1)*
C(20)	5839(3)	8513(3)	6357(2)	39(1)*
C(21)	5963(3)	7374(3)	6399(2)	51(1)*
C(22)	5759(3)	6898(3)	5731(2)	55(1)*
C(23)	5498(3)	7772(3)	5280(2)	41(1)*
C(24)	7604(2)	3583(2)	8812(1)	21(1)*
C(25)	8503(3)	4510(2)	8558(1)	24(1)*
C(26)	7758(3)	5260(2)	8030(1)	26(1)*
C(27)	6521(3)	5754(2)	8347(1)	31(1)*
C(28)	8808(3)	6198(2)	7853(2)	37(1)*
C(29)	7255(3)	4564(2)	7387(1)	38(1)*
C(30)	4120(3)	2697(3)	8985(2)	46(1)*
C(31)	4588(3)	3438(3)	9541(2)	43(1)*
C(32)	5023(3)	2782(3)	10093(2)	37(1)*
C(33)	4805(3)	1651(2)	9886(2)	34(1)*
C(34)	4273(3)	1605(3)	9206(2)	40(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

(VI)

Table 2. Bond lengths (Å)

Mo(1)-P(1)	2.322(1)	Mo(1)-P(2)	2.337(1)
Mo(1)-C(13)	1.796(2)	Mo(1)-C(19)	2.427(3)
Mo(1)-C(20)	2.407(3)	Mo(1)-C(21)	2.375(3)
Mo(1)-C(22)	2.364(3)	Mo(1)-C(23)	2.384(3)
Mo(2)-P(3)	2.314(1)	Mo(2)-P(4)	2.343(1)
Mo(2)-C(24)	1.799(2)	Mo(2)-C(30)	2.393(3)
Mo(2)-C(31)	2.363(3)	Mo(2)-C(32)	2.367(3)
Mo(2)-C(33)	2.425(3)	Mo(2)-C(34)	2.418(3)
P(1)-O(1)	1.613(2)	P(1)-O(2)	1.628(2)
P(1)-O(3)	1.608(2)	P(2)-O(4)	1.607(2)
P(2)-O(5)	1.628(2)	P(2)-O(6)	1.612(2)
P(3)-O(7)	1.600(2)	P(3)-O(8)	1.609(2)
P(3)-O(9)	1.611(2)	P(4)-O(10)	1.608(2)
P(4)-O(11)	1.607(2)	P(4)-O(12)	1.625(2)
O(1)-C(1)	1.439(3)	O(2)-C(2)	1.430(4)
O(3)-C(3)	1.436(4)	O(10)-C(10)	1.440(3)
O(11)-C(11)	1.436(3)	O(12)-C(12)	1.436(4)
O(4)-C(4)	1.451(4)	O(5)-C(5)	1.426(4)
O(6)-C(6)	1.436(4)	O(7)-C(7)	1.437(3)
O(8)-C(8)	1.418(4)	O(9)-C(9)	1.372(4)
C(13)-C(14)	1.485(3)	C(14)-C(15)	1.549(4)
C(14)-H(14a)	0.989(26)	C(14)-H(14b)	0.943(36)
C(15)-C(16)	1.534(4)	C(15)-C(17)	1.522(4)
C(15)-C(18)	1.516(4)	C(19)-C(20)	1.394(4)
C(19)-C(23)	1.403(4)	C(20)-C(21)	1.381(5)
C(21)-C(22)	1.409(5)	C(22)-C(23)	1.408(5)
C(24)-C(25)	1.486(3)	C(25)-C(26)	1.552(3)
C(25)-H(25a)	0.988(26)	C(25)-H(25b)	1.143(31)
C(26)-C(27)	1.529(4)	C(26)-C(28)	1.531(4)
C(26)-C(29)	1.526(4)	C(30)-C(31)	1.418(5)
C(30)-C(34)	1.400(5)	C(31)-C(32)	1.405(4)
C(32)-C(33)	1.404(4)	C(33)-C(34)	1.391(4)

(VI)

Table 3. Bond angles (°)

P(1)-Mo(1)-P(2)	92.9(1)	P(1)-Mo(1)-C(13)	86.3(1)
P(2)-Mo(1)-C(13)	90.4(1)	P(1)-Mo(1)-C(19)	101.8(1)
P(2)-Mo(1)-C(19)	103.1(1)	C(13)-Mo(1)-C(19)	163.7(1)
P(1)-Mo(1)-C(20)	134.3(1)	P(2)-Mo(1)-C(20)	91.1(1)
C(13)-Mo(1)-C(20)	139.2(1)	C(19)-Mo(1)-C(20)	33.5(1)
P(1)-Mo(1)-C(21)	148.8(1)	P(2)-Mo(1)-C(21)	112.3(1)
C(13)-Mo(1)-C(21)	110.5(1)	C(19)-Mo(1)-C(21)	56.0(1)
C(20)-Mo(1)-C(21)	33.6(1)	P(1)-Mo(1)-C(22)	116.4(1)
P(2)-Mo(1)-C(22)	146.1(1)	C(13)-Mo(1)-C(22)	107.3(1)
C(19)-Mo(1)-C(22)	56.5(1)	C(20)-Mo(1)-C(22)	56.5(1)
C(21)-Mo(1)-C(22)	34.6(1)	P(1)-Mo(1)-C(23)	92.1(1)
P(2)-Mo(1)-C(23)	136.5(1)	C(13)-Mo(1)-C(23)	133.0(1)
C(19)-Mo(1)-C(23)	33.9(1)	C(20)-Mo(1)-C(23)	56.3(1)
C(21)-Mo(1)-C(23)	57.0(1)	C(22)-Mo(1)-C(23)	34.5(1)
P(3)-Mo(2)-P(4)	93.5(1)	P(3)-Mo(2)-C(24)	83.0(1)
P(4)-Mo(2)-C(24)	91.8(1)	P(3)-Mo(2)-C(30)	150.3(1)
P(4)-Mo(2)-C(30)	110.1(1)	C(24)-Mo(2)-C(30)	112.9(1)
P(3)-Mo(2)-C(31)	118.7(1)	P(4)-Mo(2)-C(31)	144.5(1)
C(24)-Mo(2)-C(31)	105.7(1)	C(30)-Mo(2)-C(31)	34.7(1)
P(3)-Mo(2)-C(32)	93.3(1)	P(4)-Mo(2)-C(32)	139.3(1)
C(24)-Mo(2)-C(32)	128.9(1)	C(30)-Mo(2)-C(32)	57.1(1)
C(31)-Mo(2)-C(32)	34.6(1)	P(3)-Mo(2)-C(33)	101.1(1)
P(4)-Mo(2)-C(33)	105.3(1)	C(24)-Mo(2)-C(33)	162.0(1)
C(30)-Mo(2)-C(33)	56.2(1)	C(31)-Mo(2)-C(33)	56.8(1)
C(32)-Mo(2)-C(33)	34.1(1)	P(3)-Mo(2)-C(34)	132.9(1)
P(4)-Mo(2)-C(34)	91.0(1)	C(24)-Mo(2)-C(34)	143.7(1)
C(30)-Mo(2)-C(34)	33.8(1)	C(31)-Mo(2)-C(34)	56.8(1)
C(32)-Mo(2)-C(34)	56.3(1)	C(33)-Mo(2)-C(34)	33.4(1)
Mo(1)-P(1)-O(1)	125.7(1)	Mo(1)-P(1)-O(2)	118.5(1)
O(1)-P(1)-O(2)	94.9(1)	Mo(1)-P(1)-O(3)	112.0(1)
O(1)-P(1)-O(3)	98.7(1)	O(2)-P(1)-O(3)	103.2(1)
Mo(1)-P(2)-O(4)	115.3(1)	Mo(1)-P(2)-O(5)	119.3(1)
O(4)-P(2)-O(5)	101.7(1)	Mo(1)-P(2)-O(6)	121.1(1)
O(4)-P(2)-O(6)	104.3(1)	O(5)-P(2)-O(6)	91.2(1)
Mo(2)-P(3)-O(7)	117.7(1)	Mo(2)-P(3)-O(8)	121.0(1)
O(7)-P(3)-O(8)	102.5(1)	Mo(2)-P(3)-O(9)	118.5(1)
O(7)-P(3)-O(9)	96.6(1)	O(8)-P(3)-O(9)	95.8(1)
Mo(2)-P(4)-O(10)	125.7(1)	Mo(2)-P(4)-O(11)	110.9(1)
O(10)-P(4)-O(11)	98.9(1)	Mo(2)-P(4)-O(12)	119.4(1)
O(10)-P(4)-O(12)	95.0(1)	O(11)-P(4)-O(12)	103.1(1)
P(1)-O(1)-C(1)	120.9(2)	P(1)-O(2)-C(2)	120.3(2)
P(1)-O(3)-C(3)	122.0(2)	P(4)-O(10)-C(10)	119.9(2)
P(4)-O(11)-C(11)	122.0(2)	P(4)-O(12)-C(12)	120.4(2)
P(2)-O(4)-C(4)	121.0(2)	P(2)-O(5)-C(5)	117.5(2)
P(2)-O(6)-C(6)	119.9(2)	P(3)-O(7)-C(7)	121.6(2)
P(3)-O(8)-C(8)	119.5(2)	P(3)-O(9)-C(9)	125.2(2)
Mo(1)-C(13)-C(14)	176.7(2)	C(13)-C(14)-C(15)	115.2(2)
C(13)-C(14)-H(14a)	107.7(14)	C(15)-C(14)-H(14a)	111.5(15)
C(13)-C(14)-H(14b)	111.1(22)	C(15)-C(14)-H(14b)	106.7(22)
H(14a)-C(14)-H(14b)	104.2(27)	C(14)-C(15)-C(16)	108.4(2)
C(14)-C(15)-C(17)	110.1(2)	C(14)-C(15)-C(18)	110.0(2)
Mo(1)-C(19)-C(20)	72.5(2)	Mo(1)-C(19)-C(23)	71.4(2)
C(20)-C(19)-C(23)	107.9(3)	Mo(1)-C(20)-C(19)	74.0(2)
Mo(1)-C(20)-C(21)	71.9(2)	C(19)-C(20)-C(21)	108.8(3)
Mo(1)-C(21)-C(20)	74.5(2)	Mo(1)-C(21)-C(22)	72.2(2)
C(20)-C(21)-C(22)	108.1(3)	Mo(1)-C(22)-C(21)	73.1(2)
Mo(1)-C(22)-C(23)	73.5(2)	C(21)-C(22)-C(23)	107.5(3)
Mo(1)-C(23)-C(19)	74.7(2)	Mo(1)-C(23)-C(22)	72.0(2)
C(19)-C(23)-C(22)	107.6(3)	Mo(2)-C(24)-C(25)	172.8(2)
C(24)-C(25)-C(26)	114.7(2)	C(24)-C(25)-H(25a)	107.5(17)
C(26)-C(25)-H(25a)	109.1(17)	C(24)-C(25)-H(25b)	110.2(15)
C(26)-C(25)-H(25b)	108.0(15)	H(25a)-C(25)-H(25b)	107.1(22)
C(25)-C(26)-C(27)	109.3(2)	C(25)-C(26)-C(28)	107.8(2)
C(25)-C(26)-C(29)	109.6(2)	Mo(2)-C(30)-C(31)	71.5(2)
Mo(2)-C(30)-C(34)	74.0(2)	C(31)-C(30)-C(34)	107.5(3)
Mo(2)-C(31)-C(30)	73.8(2)	Mo(2)-C(31)-C(32)	72.9(2)
C(30)-C(31)-C(32)	107.4(3)	Mo(2)-C(32)-C(31)	72.5(2)
Mo(2)-C(32)-C(33)	75.2(2)	C(31)-C(32)-C(33)	108.3(3)
Mo(2)-C(33)-C(32)	70.7(2)	Mo(2)-C(33)-C(34)	73.0(2)
C(32)-C(33)-C(34)	107.9(3)	Mo(2)-C(34)-C(30)	72.1(2)
Mo(2)-C(34)-C(33)	73.6(2)	C(30)-C(34)-C(33)	108.9(3)

(VI)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	17(1)	22(1)	18(1)	2(1)	4(1)	2(1)
Mo(2)	15(1)	17(1)	22(1)	1(1)	2(1)	1(1)
P(1)	21(1)	28(1)	22(1)	3(1)	2(1)	-1(1)
P(2)	24(1)	23(1)	24(1)	-1(1)	5(1)	-0(1)
P(3)	20(1)	21(1)	23(1)	-1(1)	1(1)	3(1)
P(4)	24(1)	19(1)	21(1)	1(1)	2(1)	-0(1)
O(1)	20(1)	40(1)	41(1)	9(1)	3(1)	2(1)
O(2)	37(1)	38(1)	29(1)	-3(1)	-5(1)	-1(1)
O(3)	29(1)	44(1)	27(1)	14(1)	-2(1)	-5(1)
O(10)	27(1)	24(1)	32(1)	-0(1)	6(1)	4(1)
O(11)	39(1)	19(1)	28(1)	-2(1)	7(1)	-3(1)
O(12)	39(1)	34(1)	22(1)	1(1)	-2(1)	4(1)
O(4)	24(1)	33(1)	36(1)	-6(1)	12(1)	0(1)
O(5)	41(1)	38(1)	25(1)	-5(1)	3(1)	-1(1)
O(6)	47(1)	22(1)	37(1)	-2(1)	7(1)	-0(1)
O(7)	16(1)	65(1)	27(1)	-1(1)	2(1)	-2(1)
O(8)	35(1)	51(1)	27(1)	14(1)	0(1)	-1(1)
O(9)	56(1)	39(1)	81(2)	-31(1)	-38(1)	22(1)
C(1)	20(1)	62(2)	39(2)	2(1)	4(1)	-6(1)
C(2)	56(2)	46(2)	34(2)	-14(1)	3(1)	7(2)
C(3)	48(2)	89(3)	39(2)	37(2)	-14(2)	-19(2)
C(4)	34(2)	45(2)	47(2)	-6(1)	20(1)	9(1)
C(5)	64(2)	57(2)	26(2)	4(1)	2(1)	14(2)
C(6)	66(2)	27(1)	48(2)	11(1)	12(2)	10(1)
C(7)	17(1)	62(2)	47(2)	-4(2)	-4(1)	2(1)
C(8)	64(3)	46(2)	87(3)	37(2)	-26(2)	-16(2)
C(9)	42(2)	38(2)	58(2)	-22(1)	-11(2)	10(1)
C(10)	34(1)	33(1)	36(2)	-2(1)	14(1)	-2(1)
C(11)	69(2)	20(1)	38(2)	-4(1)	12(2)	-1(1)
C(12)	42(2)	47(2)	32(2)	-5(1)	-11(1)	4(1)
C(13)	22(1)	26(1)	19(1)	1(1)	2(1)	4(1)
C(14)	22(1)	30(1)	30(1)	2(1)	5(1)	-1(1)
C(15)	31(1)	26(1)	30(1)	4(1)	2(1)	-2(1)
C(16)	45(2)	31(1)	55(2)	11(1)	9(2)	-6(1)
C(17)	41(2)	31(1)	51(2)	2(1)	9(1)	7(1)
C(18)	66(2)	39(2)	32(2)	7(1)	-9(2)	-2(2)
C(19)	24(1)	36(1)	42(2)	14(1)	4(1)	-2(1)
C(20)	23(1)	57(2)	36(2)	-4(1)	-0(1)	-5(1)
C(21)	22(1)	70(2)	64(2)	38(2)	1(1)	7(1)
C(22)	23(1)	33(2)	111(3)	-0(2)	23(2)	6(1)
C(23)	23(1)	67(2)	33(2)	-8(1)	12(1)	-4(1)
C(24)	17(1)	22(1)	23(1)	-1(1)	-0(1)	3(1)
C(25)	22(1)	21(1)	29(1)	5(1)	-0(1)	-1(1)
C(26)	31(1)	23(1)	24(1)	3(1)	1(1)	3(1)
C(27)	33(1)	25(1)	34(1)	1(1)	-0(1)	7(1)
C(28)	42(2)	32(1)	39(2)	11(1)	9(1)	0(1)
C(29)	51(2)	38(2)	25(1)	-1(1)	-1(1)	7(1)
C(30)	19(1)	73(2)	46(2)	21(2)	2(1)	7(1)
C(31)	25(1)	34(1)	74(2)	11(1)	19(1)	13(1)
C(32)	22(1)	51(2)	39(2)	-7(1)	13(1)	2(1)
C(33)	24(1)	38(1)	41(2)	12(1)	13(1)	1(1)
C(34)	19(1)	47(2)	53(2)	-9(1)	10(1)	-10(1)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(\underline{h}^2\underline{a}^{*2}\underline{U}_{11} + \ldots + 2\underline{hka}^*\underline{b}^*\underline{U}_{12})$

(VI)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	-1368	7984	5472	49(9)
H(1b)	-333	7200	5846	33(8)
H(1c)	-962	6893	5099	67(11)
H(2a)	1859	5222	4263	88(13)
H(2b)	2917	5608	4881	60(10)
H(2c)	3087	6102	4156	57(10)
H(3a)	2303	9225	3614	68(11)
H(3b)	1049	9462	4050	149(22)
H(3c)	1189	8259	3739	112(16)
H(4a)	-914	8860	7136	54(10)
H(4b)	234	9845	7152	48(9)
H(4c)	334	8911	7698	54(10)
H(5a)	3602	8128	8358	79(12)
H(5b)	3723	7425	7681	64(11)
H(5c)	2260	7578	7955	156(21)
H(6a)	2336	11343	6017	72(12)
H(6b)	1424	10259	5775	100(15)
H(6c)	3009	10359	5648	95(14)
H(7a)	11985	2177	9882	96(14)
H(7b)	11114	1864	10503	119(17)
H(7c)	11425	3123	10335	72(12)
H(8a)	8265	311	11016	103(15)
H(8b)	9208	377	10398	96(16)
H(8c)	7588	372	10266	95(14)
H(9a)	8685	5265	10636	85(13)
H(9b)	7696	4346	10937	127(18)
H(9c)	7462	4667	10167	81(12)
H(10a)	10741	1346	8172	53(10)
H(10b)	9930	2355	8422	63(11)
H(10c)	9504	1773	7706	43(8)
H(11a)	6629	-1757	8650	45(9)
H(11b)	7893	-1160	8318	65(11)
H(11c)	6383	-1094	7975	63(11)
H(12a)	5582	1401	6980	83(12)
H(12b)	5347	2077	7653	39(8)
H(12c)	4828	812	7569	58(10)
H(16a)	786	3257	6382	49(9)
H(16b)	637	3745	7121	51(10)
H(16c)	1718	2848	7005	40(8)
H(17a)	4103	4607	6161	51(9)
H(17b)	2959	3763	5799	41(8)
H(17c)	3857	3406	6448	38(8)
H(18a)	3751	5429	7308	72(12)
H(18b)	3596	4219	7592	33(7)
H(18c)	2440	5059	7693	52(10)
H(19)	5449	9506	5498	55(10)
H(20)	5925	9040	6738	79(12)
H(21)	6156	6975	6812	78(12)
H(22)	5793	6121	5607	71(11)
H(23)	5306	7696	4792	61(10)
H(27a)	6846	6142	8768	47(9)
H(27b)	5870	5148	8439	29(7)
H(27c)	6073	6262	8044	30(7)
H(28a)	8411	6656	7503	44(9)
H(28b)	9590	5846	7688	36(8)
H(28c)	9108	6657	8252	62(11)
H(29a)	8064	4265	7213	41(8)
H(29b)	6791	4988	7039	38(8)
H(29c)	6635	3961	7515	39(8)
H(30)	3764	2906	8538	70(11)
H(31)	4605	4240	9541	61(10)
H(32)	5404	3060	10536	47(9)
H(33)	4991	1020	10165	42(8)
H(34)	4047	934	8932	59(10)
H(14a)	883(26)	5671(20)	6663(12)	23(6)
H(14b)	1105(39)	5120(30)	5974(19)	65(11)
H(25a)	8881(29)	4977(23)	8960(14)	28(7)
H(25b)	9430(31)	4161(24)	8312(15)	43(8)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	4237(1)	1201(1)	2921(1)	21(1)*
P(1)	5883(1)	3847(1)	2878(1)	25(1)*
P(2)	1824(1)	1047(1)	2487(1)	28(1)*
Si	3469(1)	-2252(1)	1116(1)	28(1)*
O(1)	5215(3)	4611(3)	2300(2)	33(1)*
O(2)	7507(3)	4457(3)	2524(2)	31(1)*
O(3)	6646(3)	5219(3)	3893(2)	35(1)*
O(4)	1472(3)	2074(3)	3225(2)	42(2)*
O(5)	83(3)	-624(3)	2364(2)	40(1)*
O(6)	1471(3)	1370(3)	1533(2)	36(1)*
C(1)	4984(5)	4345(4)	1326(2)	38(2)*
C(2)	8475(4)	3884(5)	2706(3)	38(2)*
C(3)	7688(5)	6936(4)	4013(3)	48(2)*
C(4)	2588(5)	3817(4)	3584(3)	52(3)*
C(5)	-381(5)	-2128(5)	1754(3)	54(2)*
C(6)	-36(5)	1190(5)	1161(3)	54(3)*
C(7)	4376(5)	1002(4)	1451(2)	27(2)*
C(8)	3762(4)	-371(4)	1761(2)	24(2)*
C(9)	5532(4)	-1673(4)	1010(3)	37(2)*
C(10)	2582(4)	-3893(4)	1647(3)	38(2)*
C(11)	2027(5)	-3074(4)	-75(2)	42(2)*
C(12)	3216(4)	319(4)	4118(2)	33(2)*
C(13)	3571(4)	-738(4)	3679(2)	30(2)*
C(14)	5302(4)	152(4)	3854(2)	26(2)*
C(15)	6361(4)	-273(4)	3630(2)	31(2)*
C(16)	8019(4)	843(4)	3956(3)	38(2)*
C(17)	8721(4)	2452(4)	4523(3)	39(2)*
C(18)	7768(4)	2942(4)	4722(2)	35(2)*
C(19)	6025(4)	1812(4)	4394(2)	28(2)*
C(20)	4702(4)	1901(4)	4532(2)	33(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-P(1)	2.351(1)	Mo-P(2)	2.358(1)
Mo-C(7)	2.258(4)	Mo-C(8)	1.955(3)
Mo-C(12)	2.341(4)	Mo-C(13)	2.369(4)
Mo-C(14)	2.439(5)	Mo-C(19)	2.426(4)
Mo-C(20)	2.339(3)	P(1)-O(1)	1.614(3)
P(1)-O(2)	1.631(3)	P(1)-O(3)	1.627(2)
P(2)-O(4)	1.610(3)	P(2)-O(5)	1.622(2)
P(2)-O(6)	1.609(3)	Si-C(8)	1.849(4)
Si-C(9)	1.879(5)	Si-C(10)	1.875(4)
Si-C(11)	1.874(4)	O(1)-C(1)	1.430(4)
O(2)-C(2)	1.426(7)	O(3)-C(3)	1.457(4)
O(4)-C(4)	1.444(4)	O(5)-C(5)	1.431(5)
O(6)-C(6)	1.453(6)	C(7)-C(8)	1.437(6)
C(7)-H(7a)	0.922(39)	C(7)-H(7b)	1.023(39)
C(12)-C(13)	1.412(7)	C(12)-C(20)	1.421(4)
C(13)-C(14)	1.422(5)	C(14)-C(15)	1.422(7)
C(14)-C(19)	1.449(5)	C(15)-C(16)	1.359(5)
C(16)-C(17)	1.423(6)	C(17)-C(18)	1.358(8)
C(18)-C(19)	1.424(5)	C(19)-C(20)	1.435(7)

Table 3. Bond angles (°)

P(1)-Mo-P(2)	91.8(1)	P(1)-Mo-C(7)	72.8(1)
P(2)-Mo-C(7)	88.8(1)	P(1)-Mo-C(8)	110.8(1)
P(2)-Mo-C(8)	96.2(1)	C(7)-Mo-C(8)	39.0(2)
P(1)-Mo-C(12)	129.3(1)	P(2)-Mo-C(12)	83.9(1)
C(7)-Mo-C(12)	156.8(1)	C(8)-Mo-C(12)	119.9(1)
P(1)-Mo-C(13)	151.8(1)	P(2)-Mo-C(13)	105.2(1)
C(7)-Mo-C(13)	128.7(1)	C(8)-Mo-C(13)	89.9(1)
C(12)-Mo-C(13)	34.9(2)	P(1)-Mo-C(14)	122.6(1)
P(2)-Mo-C(14)	138.8(1)	C(7)-Mo-C(14)	120.7(2)
C(8)-Mo-C(14)	92.1(2)	C(12)-Mo-C(14)	57.4(2)
C(13)-Mo-C(14)	34.4(1)	P(1)-Mo-C(19)	94.2(1)
P(2)-Mo-C(19)	134.2(1)	C(7)-Mo-C(19)	136.1(2)
C(8)-Mo-C(19)	123.3(2)	C(12)-Mo-C(19)	57.8(1)
C(13)-Mo-C(19)	57.8(1)	C(14)-Mo-C(19)	34.7(1)
P(1)-Mo-C(20)	97.0(1)	P(2)-Mo-C(20)	99.2(1)
C(7)-Mo-C(20)	167.3(1)	C(8)-Mo-C(20)	147.7(2)
C(12)-Mo-C(20)	35.3(1)	C(13)-Mo-C(20)	58.7(1)
C(14)-Mo-C(20)	58.1(2)	C(19)-Mo-C(20)	35.0(2)
Mo-P(1)-O(1)	124.2(1)	Mo-P(1)-O(2)	120.7(1)
O(1)-P(1)-O(2)	95.4(2)	Mo-P(1)-O(3)	112.8(1)
O(1)-P(1)-O(3)	97.4(2)	O(2)-P(1)-O(3)	101.8(1)
Mo-P(2)-O(4)	119.3(1)	Mo-P(2)-O(5)	118.0(1)
O(4)-P(2)-O(5)	91.3(1)	Mo-P(2)-O(6)	116.7(1)
O(4)-P(2)-O(6)	105.1(2)	O(5)-P(2)-O(6)	102.4(1)
C(8)-Si-C(9)	106.9(2)	C(8)-Si-C(10)	115.3(2)
C(8)-Si-C(11)	107.8(2)	P(1)-O(1)-C(1)	124.3(3)
P(1)-O(2)-C(2)	120.6(2)	P(1)-O(3)-C(3)	121.3(2)
P(2)-O(4)-C(4)	120.5(3)	P(2)-O(5)-C(5)	120.2(3)
P(2)-O(6)-C(6)	121.5(3)	Mo-C(7)-C(8)	59.0(2)
Mo-C(7)-H(7a)	114.8(22)	C(8)-C(7)-H(7a)	117.3(17)
Mo-C(7)-H(7b)	121.2(17)	C(8)-C(7)-H(7b)	115.3(25)
H(7a)-C(7)-H(7b)	116.7(30)	Mo-C(8)-Si	151.4(2)
Mo-C(8)-C(7)	81.9(2)	Si-C(8)-C(7)	123.7(3)
Mo-C(12)-C(13)	73.7(2)	Mo-C(12)-C(20)	72.3(2)
C(13)-C(12)-C(20)	109.0(4)	Mo-C(13)-C(12)	71.5(2)
Mo-C(13)-C(14)	75.5(2)	C(12)-C(13)-C(14)	108.2(3)
Mo-C(14)-C(13)	70.1(3)	Mo-C(14)-C(15)	124.2(3)
C(13)-C(14)-C(15)	133.6(3)	Mo-C(14)-C(19)	72.2(3)
C(13)-C(14)-C(19)	107.7(4)	C(15)-C(14)-C(19)	118.7(3)
C(14)-C(15)-C(16)	120.3(4)	C(15)-C(16)-C(17)	120.6(5)
C(16)-C(17)-C(18)	121.5(3)	C(17)-C(18)-C(19)	119.6(3)
Mo-C(19)-C(14)	73.2(2)	Mo-C(19)-C(18)	126.6(3)
C(14)-C(19)-C(18)	119.1(4)	Mo-C(19)-C(20)	69.2(2)
C(14)-C(19)-C(20)	107.2(3)	C(18)-C(19)-C(20)	133.5(4)
Mo-C(20)-C(12)	72.4(2)	Mo-C(20)-C(19)	75.8(2)
C(12)-C(20)-C(19)	107.7(4)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	21(1)	21(1)	24(1)	11(1)	11(1)	12(1)
P(1)	26(1)	23(1)	32(1)	12(1)	13(1)	15(1)
P(2)	23(1)	28(1)	37(1)	15(1)	15(1)	15(1)
Si	27(1)	23(1)	31(1)	9(1)	10(1)	13(1)
O(1)	40(1)	32(1)	39(1)	19(1)	17(1)	26(1)
O(2)	27(1)	28(1)	49(1)	22(1)	19(1)	17(1)
O(3)	38(1)	23(1)	40(1)	8(1)	12(1)	17(1)
O(4)	37(1)	43(2)	56(2)	15(1)	27(1)	27(1)
O(5)	23(1)	34(1)	58(2)	20(1)	17(1)	12(1)
O(6)	26(1)	43(1)	47(2)	23(1)	12(1)	23(1)
C(1)	45(2)	39(2)	44(2)	26(2)	20(2)	28(2)
C(2)	34(2)	50(2)	38(2)	23(2)	17(2)	26(2)
C(3)	48(3)	23(2)	59(3)	7(2)	4(2)	18(2)
C(4)	60(3)	43(2)	66(3)	16(2)	35(2)	36(2)
C(5)	31(2)	35(2)	78(3)	16(2)	15(2)	10(2)
C(6)	37(2)	64(3)	75(3)	35(3)	13(2)	35(2)
C(7)	31(2)	31(2)	26(2)	14(2)	10(2)	21(2)
C(8)	19(2)	28(2)	29(2)	13(2)	10(1)	14(2)
C(9)	37(2)	36(2)	40(2)	12(2)	15(2)	23(2)
C(10)	36(2)	25(2)	47(2)	11(2)	11(2)	15(2)
C(11)	42(2)	36(2)	40(2)	7(2)	10(2)	20(2)
C(12)	29(2)	46(2)	30(2)	23(2)	17(2)	20(2)
C(13)	33(2)	32(2)	29(2)	20(2)	13(2)	18(2)
C(14)	29(2)	31(2)	24(2)	18(2)	11(2)	17(2)
C(15)	38(2)	32(2)	31(2)	16(2)	10(2)	24(2)
C(16)	39(2)	49(2)	44(2)	30(2)	18(2)	31(2)
C(17)	26(2)	41(2)	45(2)	26(2)	6(2)	13(2)
C(18)	36(2)	30(2)	33(2)	15(2)	9(2)	15(2)
C(19)	33(2)	33(2)	23(2)	15(2)	11(2)	19(2)
C(20)	41(2)	38(2)	25(2)	14(2)	14(2)	24(2)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

(VII)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	5203	5326	1251	47
H(1b)	3882	3454	959	47
H(1c)	5745	4168	1124	47
H(2a)	8975	3956	2214	46
H(2b)	7808	2781	2687	46
H(2c)	9316	4542	3295	46
H(3a)	8084	7539	4664	55
H(3b)	7040	7197	3686	55
H(3c)	8604	7208	3777	55
H(4a)	2120	4195	3973	62
H(4b)	2716	4250	3083	62
H(4c)	3642	4164	3945	62
H(5a)	-1243	-2996	1905	64
H(5b)	559	-2153	1844	64
H(5c)	-757	-2249	1116	64
H(6a)	21	1598	652	60
H(6b)	-181	1788	1653	60
H(6c)	-948	69	953	60
H(9a)	5358	-2652	657	47
H(9b)	6298	-1239	1613	47
H(9c)	5965	-901	691	47
H(10a)	3334	-3574	2233	45
H(10b)	2372	-4845	1227	45
H(10c)	1570	-4119	1740	45
H(11a)	1923	-4013	-427	51
H(11b)	2505	-2257	-362	51
H(11c)	961	-3357	-58	51
H(12)	2144	17	4134	41
H(13)	2779	-1864	3323	37
H(15)	5903	-1354	3247	38
H(16)	8724	543	3803	47
H(17)	9894	3207	4769	48
H(18)	8267	4046	5083	41
H(20)	4803	2857	4848	42
H(7a)	3616(36)	1036(33)	1075(19)	13(8)
H(7b)	5468(41)	1434(37)	1306(21)	28(9)

(VIII)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	2122(1)	2138(1)	131(1)	16(1)*
P(1)	3625(1)	3371(1)	637(1)	19(1)*
P(2)	-234(1)	2330(1)	-723(1)	19(1)*
F(1)	10566(1)	5016(1)	2639(1)	43(1)*
F(2)	8886(2)	4556(1)	1595(1)	53(1)*
F(3)	9235(2)	3775(1)	2688(1)	50(1)*
F(4)	8142(2)	5114(1)	2582(1)	62(1)*
B	9204(2)	4619(2)	2382(1)	26(1)*
O(1)	4697(2)	3111(1)	1419(1)	28(1)*
O(2)	4738(2)	3698(1)	159(1)	27(1)*
O(3)	2951(2)	4312(1)	770(1)	27(1)*
O(4)	-1190(2)	3194(1)	-669(1)	26(1)*
O(5)	-268(2)	2363(1)	-1605(1)	26(1)*
O(6)	-1253(1)	1501(1)	-695(1)	25(1)*
C(1)	5819(3)	3722(2)	1818(1)	40(1)*
C(2)	4219(3)	4098(2)	-581(1)	39(1)*
C(3)	2049(3)	4438(2)	1297(2)	50(1)*
C(4)	-1574(3)	3478(2)	7(1)	54(1)*
C(5)	298(3)	3115(2)	-1938(1)	46(1)*
C(6)	-2698(2)	1436(2)	-1215(1)	36(1)*
C(7)	1369(2)	2251(1)	948(1)	18(1)*
C(8)	967(2)	2249(1)	1691(1)	24(1)*
C(9)	15(2)	1460(1)	1840(1)	22(1)*
C(10)	724(2)	574(1)	1725(1)	31(1)*
C(11)	-1511(2)	1520(2)	1315(1)	31(1)*
C(12)	-97(3)	1526(2)	2669(1)	33(1)*
C(13)	3708(2)	1481(2)	-596(1)	33(1)*
C(14)	4406(2)	1443(1)	187(1)	33(1)*
C(15)	3585(2)	882(1)	554(1)	31(1)*
C(16)	2353(2)	588(1)	-2(1)	30(1)*
C(17)	2439(2)	960(1)	-709(1)	31(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

(VIII)

Table 2. Bond lengths (Å)

Mo-P(1)	2.378(1)	Mo-P(2)	2.401(1)
Mo-C(7)	1.798(2)	Mo-C(13)	2.431(3)
Mo-C(14)	2.375(2)	Mo-C(15)	2.353(2)
Mo-C(16)	2.355(2)	Mo-C(17)	2.400(2)
Mo-H	1.738(23)	P(1)-O(1)	1.579(1)
P(1)-O(2)	1.592(2)	P(1)-O(3)	1.591(2)
P(2)-O(4)	1.596(2)	P(2)-O(5)	1.592(1)
P(2)-O(6)	1.581(1)	F(1)-B	1.392(3)
F(2)-B	1.390(3)	F(3)-B	1.380(3)
F(4)-B	1.365(3)	O(1)-C(1)	1.455(3)
O(2)-C(2)	1.445(2)	O(3)-C(3)	1.438(4)
O(4)-C(4)	1.425(3)	O(5)-C(5)	1.443(3)
O(6)-C(6)	1.462(2)	C(7)-C(8)	1.485(3)
C(8)-C(9)	1.550(3)	C(8)-H(8a)	0.917(19)
C(8)-H(8b)	1.011(23)	C(9)-C(10)	1.525(3)
C(9)-C(11)	1.525(3)	C(9)-C(12)	1.536(3)
C(13)-C(14)	1.415(3)	C(13)-C(17)	1.404(3)
C(14)-C(15)	1.415(3)	C(15)-C(16)	1.413(3)
C(16)-C(17)	1.419(3)		

Table 3. Bond angles (°)

P(1)-Mo-P(2)	121.9(1)	P(1)-Mo-C(7)	85.8(1)
P(2)-Mo-C(7)	91.8(1)	P(1)-Mo-C(13)	97.9(1)
P(2)-Mo-C(13)	107.1(1)	C(7)-Mo-C(13)	154.5(1)
P(1)-Mo-C(14)	82.8(1)	P(2)-Mo-C(14)	140.3(1)
C(7)-Mo-C(14)	122.8(1)	C(13)-Mo-C(14)	34.2(1)
P(1)-Mo-C(15)	104.5(1)	P(2)-Mo-C(15)	133.3(1)
C(7)-Mo-C(15)	97.2(1)	C(13)-Mo-C(15)	57.4(1)
C(14)-Mo-C(15)	34.8(1)	P(1)-Mo-C(16)	138.4(1)
P(2)-Mo-C(16)	98.4(1)	C(7)-Mo-C(16)	104.0(1)
C(13)-Mo-C(16)	57.3(1)	C(14)-Mo-C(16)	57.7(1)
C(15)-Mo-C(16)	34.9(1)	P(1)-Mo-C(17)	131.6(1)
P(2)-Mo-C(17)	85.2(1)	C(7)-Mo-C(17)	136.7(1)
C(13)-Mo-C(17)	33.8(1)	C(14)-Mo-C(17)	56.8(1)
C(15)-Mo-C(17)	57.5(1)	C(16)-Mo-C(17)	34.7(1)
P(1)-Mo-H	63.9(7)	P(2)-Mo-H	61.2(7)
C(7)-Mo-H	106.0(8)	C(13)-Mo-H	98.1(8)
C(14)-Mo-H	118.0(8)	C(15)-Mo-H	152.6(8)
C(16)-Mo-H	143.9(7)	C(17)-Mo-H	110.1(8)
Mo-P(1)-O(1)	110.3(1)	Mo-P(1)-O(2)	116.2(1)
O(1)-P(1)-O(2)	101.5(1)	Mo-P(1)-O(3)	121.8(1)
O(1)-P(1)-O(3)	106.0(1)	O(2)-P(1)-O(3)	98.6(1)
Mo-P(2)-O(4)	120.5(1)	Mo-P(2)-O(5)	116.3(1)
O(4)-P(2)-O(5)	99.3(1)	Mo-P(2)-O(6)	111.2(1)
O(4)-P(2)-O(6)	106.2(1)	O(5)-P(2)-O(6)	101.1(1)
F(1)-B-F(2)	109.0(2)	F(1)-B-F(3)	109.3(2)
F(2)-B-F(3)	109.2(2)	F(1)-B-F(4)	110.8(2)
F(2)-B-F(4)	108.6(2)	F(3)-B-F(4)	109.8(2)
P(1)-O(1)-C(1)	121.5(1)	P(1)-O(2)-C(2)	120.9(1)
P(1)-O(3)-C(3)	122.7(1)	P(2)-O(4)-C(4)	124.2(1)
P(2)-O(5)-C(5)	121.7(1)	P(2)-O(6)-C(6)	120.9(1)
Mo-C(7)-C(8)	170.0(1)	C(7)-C(8)-C(9)	116.4(1)
C(7)-C(8)-H(8a)	103.9(15)	C(9)-C(8)-H(8a)	111.2(14)
C(7)-C(8)-H(8b)	110.5(14)	C(9)-C(8)-H(8b)	106.9(14)
H(8a)-C(8)-H(8b)	107.6(18)	C(8)-C(9)-C(10)	110.5(2)
C(8)-C(9)-C(11)	110.3(2)	C(8)-C(9)-C(12)	107.5(2)
Mo-C(13)-C(14)	70.8(1)	Mo-C(13)-C(17)	71.9(1)
C(14)-C(13)-C(17)	107.4(2)	Mo-C(14)-C(13)	75.0(1)
Mo-C(14)-C(15)	71.7(1)	C(13)-C(14)-C(15)	108.7(2)
Mo-C(15)-C(14)	73.4(1)	Mo-C(15)-C(16)	72.6(1)
C(14)-C(15)-C(16)	107.5(2)	Mo-C(16)-C(15)	72.5(1)
Mo-C(16)-C(17)	74.4(1)	C(15)-C(16)-C(17)	107.7(2)
Mo-C(17)-C(13)	74.3(1)	Mo-C(17)-C(16)	70.9(1)
C(13)-C(17)-C(16)	108.7(2)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	16(1)	17(1)	15(1)	-1(1)	4(1)	-3(1)
P(1)	21(1)	21(1)	16(1)	-1(1)	6(1)	-5(1)
P(2)	21(1)	18(1)	17(1)	1(1)	2(1)	-1(1)
F(1)	33(1)	42(1)	45(1)	7(1)	-7(1)	-9(1)
F(2)	41(1)	90(1)	26(1)	-4(1)	6(1)	-14(1)
F(3)	48(1)	35(1)	61(1)	13(1)	-0(1)	-6(1)
F(4)	46(1)	63(1)	80(1)	-25(1)	21(1)	17(1)
B	24(1)	27(1)	27(1)	1(1)	5(1)	2(1)
O(1)	32(1)	29(1)	21(1)	-0(1)	-1(1)	-10(1)
O(2)	27(1)	31(1)	26(1)	-1(1)	13(1)	-9(1)
O(3)	34(1)	21(1)	28(1)	-3(1)	15(1)	-4(1)
O(4)	29(1)	23(1)	25(1)	1(1)	4(1)	5(1)
O(5)	35(1)	25(1)	17(1)	-0(1)	3(1)	-3(1)
O(6)	20(1)	22(1)	28(1)	3(1)	-1(1)	-5(1)
C(1)	35(1)	45(1)	33(1)	-6(1)	-5(1)	-17(1)
C(2)	49(1)	49(1)	24(1)	3(1)	16(1)	-21(1)
C(3)	68(2)	29(1)	72(2)	-9(1)	51(2)	-4(1)
C(4)	69(2)	58(2)	37(1)	5(1)	15(1)	38(1)
C(5)	78(2)	38(1)	24(1)	4(1)	14(1)	-17(1)
C(6)	24(1)	32(1)	44(1)	2(1)	-7(1)	-6(1)
C(7)	17(1)	17(1)	20(1)	-0(1)	3(1)	-4(1)
C(8)	28(1)	25(1)	20(1)	-3(1)	8(1)	-7(1)
C(9)	26(1)	23(1)	19(1)	2(1)	8(1)	-5(1)
C(10)	37(1)	25(1)	33(1)	5(1)	12(1)	-3(1)
C(11)	26(1)	37(1)	31(1)	4(1)	8(1)	-4(1)
C(12)	44(1)	34(1)	23(1)	2(1)	14(1)	-11(1)
C(13)	37(1)	32(1)	36(1)	-2(1)	21(1)	8(1)
C(14)	19(1)	32(1)	48(1)	-9(1)	6(1)	4(1)
C(15)	37(1)	27(1)	27(1)	-0(1)	2(1)	11(1)
C(16)	36(1)	18(1)	39(1)	-5(1)	13(1)	0(1)
C(17)	37(1)	27(1)	28(1)	-10(1)	4(1)	5(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	6263	3458	2300	51
H(1b)	5402	4287	1898	51
H(1c)	6544	3809	1534	51
H(2a)	5038	4351	-734	50
H(2b)	3504	4553	-581	50
H(2c)	3794	3636	-931	50
H(3a)	1977	5060	1405	61
H(3b)	2456	4123	1761	61
H(3c)	1094	4207	1071	61
H(4a)	-1796	4102	-1	65
H(4b)	-844	3339	461	65
H(4c)	-2441	3140	-3	65
H(5a)	-92	3102	-2478	57
H(5b)	1339	3043	-1827	57
H(5c)	67	3676	-1740	57
H(6a)	-3259	1039	-981	45
H(6b)	-2625	1194	-1694	45
H(6c)	-3171	2006	-1294	45
H(10a)	673	504	1193	38
H(10b)	186	104	1891	38
H(10c)	1725	550	2006	38
H(11a)	-1477	1491	791	38
H(11b)	-1910	2083	1414	38
H(11c)	-2116	1047	1423	38
H(12a)	-715	1053	2762	42
H(12b)	-512	2089	2756	42
H(12c)	854	1466	3005	42
H(13)	4040	1804	-979	41
H(14)	5290	1748	429	40
H(15)	3822	729	1083	39
H(16)	1594	205	84	36
H(17)	1745	869	-1186	37
H	1744(24)	3132(15)	-368(12)	34(6)
H(8a)	1848(23)	2261(14)	2041(12)	25(5)
H(8b)	427(25)	2814(14)	1756(13)	34(6)

TABLE 1.

ATOMIC POSITIONAL (FRACTIONAL CO-ORDINATES) PARAMETERS

WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

FOR (CP)MO(P(OME)3)2(OCOCF3)(HOCOCF3)

ATOM	X	Y	Z
MO	.25981(11)	.21048(7)	.09104(5)
P(1)	.4132(4)	.1078(3)	.16311(14)
P(2)	.4941(4)	.2473(2)	.02731(14)
F(1)	.0118(12)	.5014(6)	.1360(7)
F(2)	.2138(15)	.5938(6)	.1382(7)
F(3)	.120(2)	.5458(8)	.0473(7)
F(5')	.014(3)	.3504(13)	.3323(9)
F(6')	-.118(3)	.2498(14)	.2723(10)
F(4)	.106(2)	.2209(9)	.3380(5)
F(5)	-.0923(15)	.2836(11)	.3178(7)
F(6)	.096(2)	.3672(11)	.2878(9)
O(1)	.5602(11)	.0641(7)	.1267(5)
O(2)	.3376(11)	.0059(6)	.1882(4)
O(3)	.4683(13)	.1447(7)	.2359(5)
O(4)	.6581(3)	.2543(5)	.0656(4)
O(5)	.5321(3)	.1680(5)	-.0291(4)
O(6)	.5013(3)	.3478(5)	-.0106(4)
O(7)	.1967(10)	.3598(6)	.0817(5)
O(8)	.3822(14)	.4378(7)	.1410(6)
O(9')	.157(3)	.223(2)	.1921(12)
O(9)	.1526(15)	.2528(9)	.1832(6)
O(10')	.263(4)	.330(3)	.2537(15)
O(10)	-.036(3)	.167(2)	.2123(8)
C(1)	.674(2)	.0043(12)	.1623(8)
C(2)	.255(3)	-.0054(11)	.2502(7)
C(3)	.540(3)	.2311(15)	.2498(8)
C(4)	.7210(15)	.3382(9)	.0954(7)
C(5)	.6704(13)	.1751(9)	-.0708(6)
C(6)	.3849(15)	.3781(10)	-.0595(8)
C(7)	.261(2)	.4306(9)	.1125(7)
C(8)	.147(3)	.5187(10)	.1879(10)
C(9')	.153(4)	.271(3)	.242(2)
C(9)	.057(2)	.2324(14)	.2206(10)
C(10)	.0419(15)	.2779(10)	.2926(6)
C(11)	.0089(12)	.1441(8)	.0649(6)
C(12)	.0503(12)	.1996(8)	.0107(6)
C(13)	.1923(13)	.1622(8)	-.0175(6)
C(14)	.2370(13)	.0814(8)	.0218(5)
C(15)	.1226(12)	.0732(8)	.0743(5)

TABLE 2.

THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

FOR (CP)MO(P(OME)3)2(OCOCF3)(HOCOCF3)

ANISOTROPIC PARAMETERS IN THE FORM EXP(-2 **2(U11*A **2*H**2 + U22*B **2*K**2 + U33*C **2*L**2 + 2U23*B *C *K*L + 2U13*A *C *H*L + 2U12*A *B *H*K))

FOR ISOTROPIC PARAMETERS U11 = UISO

ATOM	U11	U22	U33	U23	U13	U12 (A)
MO	.0279(5)	.0204(5)	.0345(5)	-.0000(5)	.0043(4)	.0010(5)
P(1)	.038(2)	.042(2)	.0236(15)	-.0031(14)	.0053(13)	-.0008(15)
P(2)	.033(2)	.0183(13)	.034(2)	-.0008(12)	.0023(13)	.0002(12)
F(1)	.114(8)	.034(5)	.247(13)	.010(7)	.128(9)	.011(5)
F(2)	.167(11)	.030(5)	.229(13)	-.046(7)	.067(11)	-.013(7)
F(3)	.162(12)	.075(8)	.189(13)	.043(8)	.052(11)	.069(9)
F(5')	.035(5)					
F(6')	.040(6)					
F(4)	.233(14)	.133(12)	.054(6)	-.050(7)	-.052(8)	.142(11)
F(5)	.077(9)	.102(11)	.090(10)	-.020(9)	.060(8)	-.009(9)
F(6)	.18(2)	.102(12)	.148(14)	-.090(11)	.121(13)	-.110(12)
O(1)	.069(7)	.038(7)	.044(6)	.028(5)	.027(5)	.034(6)
O(2)	.067(6)	.051(6)	.042(5)	.003(5)	.001(5)	-.009(5)
O(3)	.104(9)	.059(7)	.051(6)	.004(5)	-.014(6)	-.033(7)
O(4)	.039(5)	.024(4)	.037(5)	-.004(4)	.004(4)	-.000(4)
O(5)	.042(5)	.029(4)	.026(4)	-.006(4)	.013(4)	-.007(4)
O(6)	.041(5)	.019(4)	.058(6)	.006(4)	.002(4)	-.001(4)
O(7)	.039(5)	.026(5)	.103(8)	-.012(5)	.000(5)	.011(4)
O(8)	.087(9)	.043(6)	.102(9)	-.026(6)	-.012(7)	-.014(6)
O(9')	.045(7)					
O(9)	.055(9)	.052(8)	.044(8)	-.030(7)	.021(7)	.002(7)
O(10')	.067(9)					
O(10)	.13(2)	.29(3)	.045(9)	-.055(14)	.042(11)	-.11(2)
C(1)	.063(10)	.034(13)	.074(11)	.041(10)	.027(9)	.038(9)
C(2)	.17(2)	.053(10)	.050(9)	.006(8)	.046(11)	-.026(12)
C(3)	.22(3)	.14(2)	.057(10)	.024(11)	-.044(13)	-.16(2)
C(4)	.059(9)	.032(7)	.054(8)	-.011(7)	-.005(7)	-.015(7)
C(5)	.043(7)	.039(7)	.037(7)	-.004(6)	.014(6)	-.004(6)
C(6)	.053(9)	.045(9)	.079(10)	.029(8)	-.006(8)	-.000(7)
C(7)	.071(10)	.017(6)	.055(9)	-.007(6)	.038(8)	-.002(7)
C(8)	.110(15)	.014(7)	.14(2)	-.008(9)	.070(14)	-.003(9)
C(9')	.028(8)					
C(9)	.031(10)	.069(15)	.048(11)	.010(10)	-.014(9)	-.030(10)
C(10)	.055(8)	.041(8)	.045(7)	-.015(7)	.005(7)	.007(7)
C(11)	.028(6)	.029(6)	.040(7)	-.002(5)	.002(5)	-.004(5)
C(12)	.029(6)	.016(6)	.072(8)	-.006(6)	-.006(6)	.004(5)
C(13)	.045(7)	.035(7)	.031(7)	.002(6)	-.005(6)	-.006(6)
C(14)	.038(7)	.025(6)	.028(6)	-.012(5)	-.002(5)	-.005(5)
C(15)	.027(6)	.036(7)	.023(6)	.002(5)	-.002(5)	-.005(5)

TABLE 3.

BOND LENGTHS (A) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

FOR (CP)M0(P(OME)3)2(OCOCF3)(HOCOCF3)

M0	-P(1)	2.433(3)	M0	-P(2)	2.413(3)
M0	-O(7)	2.157(8)	M0	-O(9')	2.18(3)
M0	-O(9)	2.139(12)	M0	-C(11)	2.384(10)
M0	-C(12)	2.333(11)	M0	-C(13)	2.302(11)
M0	-C(14)	2.251(10)	M0	-C(15)	2.264(10)
P(1)	-O(1)	1.552(9)	P(1)	-O(2)	1.625(9)
P(1)	-O(3)	1.571(9)	P(2)	-O(4)	1.589(8)
P(2)	-O(5)	1.536(7)	P(2)	-O(6)	1.587(8)
F(1)	-C(8)	1.33(3)	F(5')	-F(5)	1.33(3)
F(5')	-F(6)	1.14(3)	F(5')	-C(10)	1.30(3)
F(6')	-O(10)	1.75(3)	F(6')	-C(9)	1.77(3)
F(5)	-F(6')	1.02(3)	F(5)	-C(10)	1.25(2)
F(6)	-O(10')	1.65(4)	F(6)	-C(9')	1.69(4)
F(6)	-C(10)	1.33(2)	O(1)	-C(1)	1.46(2)
O(2)	-C(2)	1.42(2)	O(3)	-C(3)	1.41(3)
O(4)	-C(4)	1.412(14)	O(5)	-C(5)	1.439(13)
O(6)	-C(6)	1.441(15)	O(7)	-C(7)	1.288(15)
O(9')	-O(9)	.45(3)	O(9')	-C(9')	1.18(4)
O(9')	-C(9)	1.02(3)	O(9)	-C(9')	1.18(4)
O(9)	-C(9)	1.13(3)	O(10')	-C(9')	1.27(5)
O(10)	-C(9)	1.22(3)	C(7)	-O(8)	1.17(2)
C(8)	-F(2)	1.32(2)	C(8)	-F(3)	1.27(3)
C(8)	-C(7)	1.57(2)	C(9)	-C(9')	1.06(4)
C(10)	-F(6')	1.41(3)	C(10)	-F(4)	1.31(2)
C(10)	-C(9')	1.33(4)	C(10)	-C(9)	1.55(3)
C(11)	-C(12)	1.351(15)	C(11)	-C(15)	1.397(14)
C(12)	-C(13)	1.430(15)	C(13)	-C(14)	1.416(15)
C(14)	-C(15)	1.432(14)			

TABLE 4. CONTINUED

O(9)	-C(9)	-C(9')	65.(3)	O(10)	-C(9)	-C(9')	158.(3)
F(6')	-C(9)	-C(10)	49.8(9)	O(9')	-C(9)	-C(10)	128.(2)
O(9)	-C(9)	-C(10)	123.(2)	O(10)	-C(9)	-C(10)	111.7(15)
C(9')	-C(9)	-C(10)	60.(2)	F(5')	-C(10)	-F(6')	102.5(14)
F(5')	-C(10)	-F(4)	98.8(12)	F(6')	-C(10)	-F(4)	113.8(13)
F(5')	-C(10)	-F(5)	63.0(11)	F(6')	-C(10)	-F(5)	44.5(10)
F(4)	-C(10)	-F(5)	98.6(12)	F(5')	-C(10)	-F(6)	51.4(11)
F(6')	-C(10)	-F(6)	123.9(14)	F(4)	-C(10)	-F(6)	118.1(13)
F(5)	-C(10)	-F(6)	106.6(13)	F(5')	-C(10)	-C(9')	128.(2)
F(6')	-C(10)	-C(9')	114.(2)	F(4)	-C(10)	-C(9')	99.(2)
F(5)	-C(10)	-C(9')	157.(2)	F(6)	-C(10)	-C(9')	77.(2)
F(5')	-C(10)	-C(9)	151.5(14)	F(6')	-C(10)	-C(9)	73.2(11)
F(4)	-C(10)	-C(9)	109.6(12)	F(5)	-C(10)	-C(9)	117.6(12)
F(6)	-C(10)	-C(9)	106.8(12)	C(9')	-C(10)	-C(9)	42.0(15)
M0	-C(11)	-C(12)	73.4(6)	M0	-C(11)	-C(15)	67.9(6)
C(12)	-C(11)	-C(15)	109.3(9)	M0	-C(12)	-C(11)	73.5(6)
M0	-C(12)	-C(13)	69.2(6)	C(11)	-C(12)	-C(13)	108.4(9)
M0	-C(13)	-C(12)	75.3(6)	M0	-C(13)	-C(14)	70.4(6)
C(12)	-C(13)	-C(14)	107.9(9)	M0	-C(14)	-C(13)	73.5(6)
M0	-C(14)	-C(15)	71.7(6)	C(13)	-C(14)	-C(15)	106.8(9)
M0	-C(15)	-C(11)	77.3(6)	M0	-C(15)	-C(14)	71.4(6)
C(11)	-C(15)	-C(14)	108.4(9)				

TABLE 4.

INTER BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

FOR (CP)M0(P(OME)3)2(OCOCF3)(HOCOCF3)

P(1)	-M0	-P(2)	89.8(1)	P(1)	-M0	-O(7)	139.8(2)
P(2)	-M0	-O(7)	87.6(2)	P(1)	-M0	-O(9')	74.6(6)
P(2)	-M0	-O(9')	142.2(6)	O(7)	-M0	-O(9')	84.1(7)
P(1)	-M0	-O(9)	84.3(3)	P(2)	-M0	-O(9)	138.1(3)
O(7)	-M0	-O(9)	72.2(4)	O(9')	-M0	-O(9)	11.9(7)
P(1)	-M0	-C(11)	112.3(3)	P(2)	-M0	-C(11)	135.6(3)
O(7)	-M0	-C(11)	97.6(3)	O(9')	-M0	-C(11)	82.1(7)
O(9)	-M0	-C(11)	84.4(4)	P(1)	-M0	-C(12)	139.1(3)
P(2)	-M0	-C(12)	107.0(3)	O(7)	-M0	-C(12)	79.6(3)
O(9')	-M0	-C(12)	107.6(7)	O(9)	-M0	-C(12)	104.9(4)
C(11)	-M0	-C(12)	33.2(4)	P(1)	-M0	-C(13)	120.1(3)
P(2)	-M0	-C(13)	77.9(3)	O(7)	-M0	-C(13)	98.2(4)
O(9')	-M0	-C(13)	139.8(7)	O(9)	-M0	-C(13)	139.9(4)
C(11)	-M0	-C(13)	57.7(4)	C(12)	-M0	-C(13)	35.5(4)
P(1)	-M0	-C(14)	85.5(3)	P(2)	-M0	-C(14)	85.9(3)
O(7)	-M0	-C(14)	134.1(3)	O(9')	-M0	-C(14)	125.2(7)
O(9)	-M0	-C(14)	134.4(4)	C(11)	-M0	-C(14)	59.1(4)
C(12)	-M0	-C(14)	59.3(4)	C(13)	-M0	-C(14)	36.1(4)
P(1)	-M0	-C(15)	81.7(3)	P(2)	-M0	-C(15)	122.4(3)
O(7)	-M0	-C(15)	132.4(3)	O(9')	-M0	-C(15)	89.2(7)
O(9)	-M0	-C(15)	97.5(4)	C(11)	-M0	-C(15)	34.9(3)
C(12)	-M0	-C(15)	57.8(3)	C(13)	-M0	-C(15)	59.7(4)
M0	-P(1)	-O(1)	113.4(3)	M0	-P(1)	-O(2)	118.8(3)
O(1)	-P(1)	-O(2)	97.2(5)	M0	-P(1)	-O(3)	118.1(4)
O(1)	-P(1)	-O(3)	109.8(5)	O(2)	-P(1)	-O(3)	96.7(5)
M0	-P(2)	-O(4)	119.8(3)	M0	-P(2)	-O(5)	112.4(3)
O(4)	-P(2)	-O(5)	100.9(4)	M0	-P(2)	-O(6)	117.6(3)
O(4)	-P(2)	-O(6)	97.5(4)	O(5)	-P(2)	-O(6)	106.2(4)
F(5)	-F(5')	-F(6)	113.(2)	F(5)	-F(5')	-C(10)	56.7(11)
F(6)	-F(5')	-C(10)	65.7(13)	F(5)	-F(6')	-O(10)	146.(2)
F(5)	-F(6')	-C(9)	116.(2)	O(10)	-F(6')	-C(9)	40.3(10)
F(5)	-F(6')	-C(10)	59.3(13)	O(10)	-F(6')	-C(10)	92.0(13)
O(9)	-F(6')	-C(10)	57.0(10)	F(5')	-F(5)	-F(6')	128.(2)
F(5')	-F(5)	-C(10)	60.3(11)	F(6')	-F(5)	-C(10)	76.3(14)
F(5')	-F(6)	-O(10')	141.(2)	F(5')	-F(6)	-C(9')	115.(2)
O(10')	-F(6)	-C(9')	44.6(15)	F(5')	-F(6)	-C(10)	62.8(13)
O(10')	-F(6)	-C(10)	92.8(14)	C(9')	-F(6)	-C(10)	52.6(13)
P(1)	-O(1)	-C(1)	122.5(8)	P(1)	-O(2)	-C(2)	123.7(8)
P(1)	-O(3)	-C(3)	125.7(9)	P(2)	-O(4)	-C(4)	125.5(7)
P(2)	-O(5)	-C(5)	120.9(7)	P(2)	-O(6)	-C(6)	122.9(7)
M0	-O(7)	-C(7)	126.6(8)	M0	-O(9')	-O(9)	75.(4)
M0	-O(9')	-C(9')	144.(3)	O(9)	-O(9')	-C(9')	79.(4)
M0	-O(9')	-C(9)	147.(3)	O(9)	-O(9')	-C(9)	92.(4)
O(9')	-O(9')	-C(9)	57.(3)	M0	-O(9)	-O(9')	93.(4)
M0	-O(9)	-C(9')	153.(2)	O(9')	-O(9)	-C(9')	79.(4)
M0	-O(9)	-C(9)	142.9(13)	O(9')	-O(9)	-C(9)	65.(4)
O(9')	-O(9)	-C(9)	55.(2)	F(6)	-O(10')	-C(9')	69.(2)
F(6')	-O(10)	-C(9)	70.2(15)	O(3)	-H(3C)	-C(3)	56.8(8)
O(7)	-C(7)	-O(8)	131.8(12)	O(7)	-C(7)	-C(8)	108.8(12)
O(8)	-C(7)	-C(8)	120.2(12)	F(1)	-C(8)	-F(2)	109.4(14)
F(1)	-C(8)	-F(3)	107.(2)	F(2)	-C(8)	-F(3)	105.1(12)
F(1)	-C(8)	-C(7)	112.5(11)	F(2)	-C(8)	-C(7)	109.8(14)
F(3)	-C(8)	-C(7)	113.4(14)	F(6)	-C(9')	-O(9')	153.(3)
F(6)	-C(9')	-O(9)	133.(3)	O(9')	-C(9')	-O(9)	22.8(14)
F(6)	-C(9')	-O(10')	66.(2)	O(9')	-C(9')	-O(10')	120.(4)
O(9)	-C(9')	-O(10')	108.(3)	F(6)	-C(9')	-C(9)	113.(3)
O(9')	-C(9')	-C(9)	54.(3)	O(9)	-C(9')	-C(9)	60.(2)
O(10')	-C(9')	-C(9)	165.(4)	F(6)	-C(9')	-C(10)	50.1(13)
O(9')	-C(9')	-C(10)	131.(3)	O(9)	-C(9')	-C(10)	136.(3)
O(10')	-C(9')	-C(10)	109.(3)	C(9)	-C(9')	-C(10)	78.(3)
F(6')	-C(9)	-O(9')	178.(3)	F(6')	-C(9)	-O(9)	157.(2)
O(9')	-C(9)	-O(9)	23.(2)	F(6')	-C(9)	-O(10)	69.5(13)
O(9')	-C(9)	-O(10)	112.(3)	O(9)	-C(9)	-O(10)	125.(2)
F(6')	-C(9)	-C(9')	109.(3)	O(9')	-C(9)	-C(9')	69.(3)

TABLE 1. CONTINUED

H(1A)	.760(2)	-.0170(12)	.1344(8)
H(1B)	.618(2)	-.0503(12)	.1709(8)
H(1C)	.715(2)	.0405(12)	.2002(8)
H(2A)	.191(3)	-.0609(11)	.2595(7)
H(2B)	.192(3)	.0514(11)	.2544(7)
H(2C)	.348(3)	-.0027(11)	.2823(7)
H(3A)	.613(3)	.2455(15)	.2856(8)
H(3B)	.488(3)	.2889(15)	.2359(8)
H(3C)	.595(3)	.2042(15)	.2116(8)
H(4A)	.8080(15)	.3200(9)	.1238(7)
H(4B)	.6531(15)	.3804(9)	.1204(7)
H(4C)	.7592(15)	.3704(9)	.0555(7)
H(5A)	.6448(13)	.1380(9)	-.1104(6)
H(5B)	.7608(13)	.1473(9)	-.0486(6)
H(5C)	.6944(13)	.2397(9)	-.0842(6)
H(6A)	.4023(15)	.4430(10)	-.0740(8)
H(6B)	.2882(15)	.3746(10)	-.0345(8)
H(6C)	.3791(15)	.3369(10)	-.0986(8)
H(11)	-.0837(12)	.1523(8)	.0320(6)
H(12)	-.0062(12)	.2545(8)	-.0058(6)
H(13)	.2474(13)	.1874(8)	-.0562(6)
H(14)	.3259(13)	.0405(8)	.0143(5)
H(15)	.1238(12)	.0269(8)	.1112(5)

2. CONTINUED

.07992
.07992
.07992
.09965
.09965
.09965
.15035
.15035
.15035
.05940
.05940
.05940
.04653
.04653
.04653
.06934
.06934
.06934
.03803
.04650
.04601
.03262
.03374

TABLE 3. CONTINUED

O(3)	-H(3C)	1.43(3)	C(1)	-H(1A)	.960
C(1)	-H(1B)	.950	C(1)	-H(1C)	.960
C(2)	-H(2A)	.950	C(2)	-H(2B)	.960
C(2)	-H(2C)	.950	C(3)	-H(3A)	.960
C(3)	-H(3B)	.950	C(3)	-H(3C)	.960
C(4)	-H(4A)	.950	C(4)	-H(4B)	.960
C(4)	-H(4C)	.950	C(5)	-H(5A)	.960
C(5)	-H(5B)	.950	C(5)	-H(5C)	.960
C(6)	-H(6A)	.950	C(6)	-H(6B)	.960
C(6)	-H(6C)	.950	C(11)	-H(11)	.960
C(12)	-H(12)	.950	C(13)	-H(13)	.960
C(14)	-H(14)	.950	C(15)	-H(15)	.960

TABLE 4. CONTINUED

O(1)	-O(3)	-H(3C)	95.2(8)
O(1)	-C(1)	-H(1A)	114.4(7)
H(1A)	-C(1)	-H(1B)	109.5
H(1A)	-C(1)	-H(1C)	109.5
O(2)	-C(2)	-H(2A)	122.2(7)
H(2A)	-C(2)	-H(2B)	109.5
H(2A)	-C(2)	-H(2C)	109.5
O(3)	-C(3)	-H(3A)	129.3(8)
H(3A)	-C(3)	-H(3B)	109.5
H(3A)	-C(3)	-H(3C)	109.5
O(4)	-C(4)	-H(4A)	108.3(6)
H(4A)	-C(4)	-H(4B)	109.5
H(4A)	-C(4)	-H(4C)	109.5
O(5)	-C(5)	-H(5A)	103.4(5)
H(5A)	-C(5)	-H(5B)	109.5
H(5A)	-C(5)	-H(5C)	109.5
O(6)	-C(6)	-H(6A)	111.6(6)
H(6A)	-C(6)	-H(6B)	109.5
H(6A)	-C(6)	-H(6C)	109.5
HO	-C(11)	-H(11)	125.0(2)
H(11)	-C(11)	-C(15)	125.3(6)
C(11)	-C(12)	-H(12)	125.8(6)
HO	-C(13)	-H(13)	120.1(3)
H(13)	-C(13)	-C(14)	126.1(6)
C(13)	-C(14)	-H(14)	127.0(6)
HO	-C(15)	-H(15)	117.4(2)
C(14)	-C(15)	-H(15)	125.8(6)

C(3)	-O(3)	-H(3C)	38.5(6)
O(1)	-C(1)	-H(1B)	106.1(7)
O(1)	-C(1)	-H(1C)	107.8(7)
H(1B)	-C(1)	-H(1C)	109.5
O(2)	-C(2)	-H(2B)	105.2(7)
O(2)	-C(2)	-H(2C)	100.3(8)
H(2B)	-C(2)	-H(2C)	109.5
O(3)	-C(3)	-H(3B)	116.1(10)
O(3)	-C(3)	-H(3C)	75.5(9)
H(3B)	-C(3)	-H(3C)	109.5
O(4)	-C(4)	-H(4B)	119.3(6)
O(4)	-C(4)	-H(4C)	100.3(6)
H(4B)	-C(4)	-H(4C)	109.5
O(5)	-C(5)	-H(5B)	111.5(5)
O(5)	-C(5)	-H(5C)	113.3(5)
H(5B)	-C(5)	-H(5C)	109.5
O(6)	-C(6)	-H(6B)	103.7(6)
O(6)	-C(6)	-H(6C)	113.8(6)
H(6B)	-C(6)	-H(6C)	109.5
H(11)	-C(11)	-C(12)	125.4(6)
HO	-C(12)	-H(12)	123.1(2)
H(12)	-C(12)	-C(13)	125.8(6)
C(12)	-C(13)	-H(13)	126.1(6)
HO	-C(14)	-H(14)	119.8(3)
H(14)	-C(14)	-C(15)	127.0(6)
C(11)	-C(15)	-H(15)	125.8(6)

(X)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	-22(1)	-31(1)	457(1)	34(1)*
P	807(2)	1201(1)	1296(1)	63(1)*
O(1)	2451(4)	1368(3)	1204(3)	69(2)*
O(2a)	325(7)	1405(4)	2170(3)	59(2)
O(2b)	1018(14)	612(7)	2096(5)	68(4)
O(3a)	144(9)	2129(4)	886(4)	69(2)
O(3b)	-129(14)	2084(5)	1539(7)	82(5)
N(1)	-2256(7)	-163(5)	2579(3)	87(3)*
N(2)	-3449(8)	1659(5)	673(5)	101(3)*
N(3)	-2355(7)	-2204(4)	1244(4)	78(2)*
N(4)	-4072(7)	-445(6)	-521(3)	92(3)*
C(1)	-2088(5)	213(4)	1116(3)	40(1)*
C(2)	-2220(5)	-615(4)	590(3)	40(2)*
C(3)	765(5)	-827(4)	1114(3)	42(2)*
C(4)	1402(7)	-1521(5)	1628(4)	63(2)*
C(5)	3021(7)	-1710(4)	1563(4)	58(2)*
C(6)	3417(11)	-2468(6)	2161(6)	104(4)*
C(7)	3893(8)	-843(6)	1748(6)	106(4)*
C(8)	3403(9)	-2026(5)	761(5)	81(3)*
C(11)	-2158(6)	18(5)	1932(3)	54(2)*
C(12)	-2850(7)	1013(4)	882(4)	56(2)*
C(23)	-2284(6)	-1500(4)	956(3)	48(2)*
C(24)	-3248(7)	-514(4)	-36(4)	56(2)*
C(31)	3314(11)	1950(6)	1666(6)	116(4)*
C(32)	844(11)	917(6)	2816(5)	106(4)*
C(33)	-127(12)	2944(6)	1180(6)	152(6)*
C(41)	-261(10)	-334(5)	-907(4)	71(3)*
C(42)	1090(8)	-589(5)	-677(4)	62(2)*
C(43)	1856(7)	191(5)	-441(3)	62(2)*
C(44)	914(9)	954(4)	-550(4)	68(3)*
C(45)	-402(8)	602(6)	-841(4)	64(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-P	2.427(2)	Mo-C(1)	2.243(5)
Mo-C(2)	2.210(5)	Mo-C(3)	1.774(5)
Mo-C(41)	2.395(6)	Mo-C(42)	2.346(7)
Mo-C(43)	2.341(6)	Mo-C(44)	2.409(7)
Mo-C(45)	2.438(7)	P-O(1)	1.543(4)
P-O(2a)	1.593(6)	P-O(2b)	1.632(9)
P-O(3a)	1.644(7)	P-O(3b)	1.605(10)
O(1)-C(31)	1.408(11)	O(2a)-O(2b)	1.327(13)
O(2a)-O(3b)	1.526(12)	O(2a)-C(32)	1.402(10)
O(2b)-C(32)	1.323(12)	O(3a)-O(3b)	1.151(14)
O(3a)-C(33)	1.315(11)	O(3b)-C(33)	1.398(13)
N(1)-C(11)	1.147(8)	N(2)-C(12)	1.150(10)
N(3)-C(23)	1.142(8)	N(4)-C(24)	1.132(9)
C(1)-C(2)	1.512(7)	C(1)-C(11)	1.432(8)
C(1)-C(12)	1.419(8)	C(2)-C(23)	1.437(8)
C(2)-C(24)	1.441(8)	C(3)-C(4)	1.466(9)
C(4)-C(5)	1.522(9)	C(5)-C(6)	1.553(11)
C(5)-C(7)	1.532(11)	C(5)-C(8)	1.496(11)
C(41)-C(42)	1.358(11)	C(41)-C(45)	1.376(11)
C(42)-C(43)	1.399(10)	C(43)-C(44)	1.425(10)
C(44)-C(45)	1.408(11)		

(X)

Table 3. Bond angles (°)

P-Mo-C(1)	81.4(1)	P-Mo-C(2)	120.9(1)
C(1)-Mo-C(2)	39.7(2)	P-Mo-C(3)	88.7(2)
C(1)-Mo-C(3)	97.5(2)	C(2)-Mo-C(3)	93.3(2)
P-Mo-C(41)	138.3(2)	C(1)-Mo-C(41)	116.4(2)
C(2)-Mo-C(41)	86.9(2)	C(3)-Mo-C(41)	122.6(3)
P-Mo-C(42)	127.7(2)	C(1)-Mo-C(42)	147.6(2)
C(2)-Mo-C(42)	110.7(2)	C(3)-Mo-C(42)	97.0(2)
C(41)-Mo-C(42)	33.3(3)	P-Mo-C(43)	93.2(2)
C(1)-Mo-C(43)	159.7(2)	C(2)-Mo-C(43)	143.1(2)
C(3)-Mo-C(43)	101.9(2)	C(41)-Mo-C(43)	56.6(3)
C(42)-Mo-C(43)	34.7(2)	P-Mo-C(44)	82.7(2)
C(1)-Mo-C(44)	124.9(2)	C(2)-Mo-C(44)	129.2(2)
C(3)-Mo-C(44)	134.5(3)	C(41)-Mo-C(44)	56.0(3)
C(42)-Mo-C(44)	56.9(2)	C(43)-Mo-C(44)	34.9(3)
P-Mo-C(45)	107.9(2)	C(1)-Mo-C(45)	106.2(2)
C(2)-Mo-C(45)	96.2(2)	C(3)-Mo-C(45)	152.6(2)
C(41)-Mo-C(45)	33.1(3)	C(42)-Mo-C(45)	55.6(3)
C(43)-Mo-C(45)	56.7(2)	C(44)-Mo-C(45)	33.8(3)
Mo-P-O(1)	111.5(2)	Mo-P-O(2a)	127.5(2)
O(1)-P-O(2a)	110.0(3)	Mo-P-O(2b)	98.5(4)
O(1)-P-O(2b)	93.0(5)	O(2a)-P-O(2b)	48.6(4)
Mo-P-O(3a)	103.8(3)	O(1)-P-O(3a)	101.0(3)
O(2a)-P-O(3a)	98.4(3)	O(2b)-P-O(3a)	147.0(5)
Mo-P-O(3b)	125.4(4)	O(1)-P-O(3b)	115.3(5)
O(2a)-P-O(3b)	57.0(5)	O(2b)-P-O(3b)	105.5(6)
O(3a)-P-O(3b)	41.5(5)	P-O(1)-C(31)	126.4(5)
P-O(2a)-O(2b)	67.2(4)	P-O(2a)-O(3b)	61.9(5)
O(2b)-O(2a)-O(3b)	129.0(7)	P-O(2a)-C(32)	123.7(6)
O(2b)-O(2a)-C(32)	57.9(6)	O(3b)-O(2a)-C(32)	169.9(7)
P-O(2b)-O(2a)	64.2(5)	P-O(2b)-C(32)	126.5(8)
O(2a)-O(2b)-C(32)	63.9(6)	P-O(3a)-O(3b)	67.5(6)
P-O(3a)-C(33)	130.6(7)	O(3b)-O(3a)-C(33)	68.7(7)
P-O(3b)-O(2a)	61.1(4)	P-O(3b)-O(3a)	71.0(7)
O(2a)-O(3b)-O(3a)	132.0(9)	P-O(3b)-C(33)	127.2(10)
O(2a)-O(3b)-C(33)	153.5(10)	O(3a)-O(3b)-C(33)	61.2(7)
Mo-C(1)-C(2)	69.0(3)	Mo-C(1)-C(11)	120.0(4)
C(2)-C(1)-C(11)	114.9(5)	Mo-C(1)-C(12)	114.1(4)
C(2)-C(1)-C(12)	116.6(5)	C(11)-C(1)-C(12)	114.7(5)
Mo-C(2)-C(1)	71.3(3)	Mo-C(2)-C(23)	115.4(4)
C(1)-C(2)-C(23)	117.4(5)	Mo-C(2)-C(24)	119.1(4)
C(1)-C(2)-C(24)	114.6(5)	C(23)-C(2)-C(24)	113.0(5)
Mo-C(3)-C(4)	177.1(5)	C(3)-C(4)-C(5)	118.3(5)
C(4)-C(5)-C(6)	108.1(6)	C(4)-C(5)-C(7)	110.5(6)
C(4)-C(5)-C(8)	110.7(6)	N(1)-C(11)-C(1)	177.3(7)
N(2)-C(12)-C(1)	178.0(8)	N(3)-C(23)-C(2)	179.0(6)
N(4)-C(24)-C(2)	178.8(7)	O(2a)-C(32)-O(2b)	58.2(6)
O(3a)-C(33)-O(3b)	50.1(7)	Mo-C(41)-C(42)	71.4(4)
Mo-C(41)-C(45)	75.2(4)	C(42)-C(41)-C(45)	109.5(7)
Mo-C(42)-C(41)	75.3(4)	Mo-C(42)-C(43)	72.4(4)
C(41)-C(42)-C(43)	109.0(7)	Mo-C(43)-C(42)	72.8(4)
Mo-C(43)-C(44)	75.2(4)	C(42)-C(43)-C(44)	106.8(6)
Mo-C(44)-C(43)	70.0(4)	Mo-C(44)-C(45)	74.2(4)
C(43)-C(44)-C(45)	106.7(6)	Mo-C(45)-C(41)	71.8(4)
Mo-C(45)-C(44)	72.0(4)	C(41)-C(45)-C(44)	108.1(7)

(X)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	34(1)	33(1)	36(1)	3(1)	2(1)	-1(1)
P	47(1)	82(1)	60(1)	-26(1)	12(1)	-21(1)
O(1)	46(2)	70(3)	91(3)	-9(3)	8(2)	-22(2)
N(1)	86(4)	124(6)	51(3)	-13(4)	17(3)	-30(4)
N(2)	88(5)	74(4)	142(6)	-1(4)	-1(5)	32(4)
N(3)	74(4)	48(3)	113(5)	19(3)	6(4)	-5(3)
N(4)	60(4)	156(7)	59(4)	3(4)	-18(3)	-10(4)
C(1)	35(2)	44(3)	41(3)	1(2)	1(2)	2(2)
C(2)	34(2)	40(2)	48(3)	3(2)	-3(2)	-1(2)
C(3)	27(2)	45(3)	54(3)	8(2)	1(2)	-4(2)
C(4)	52(4)	68(4)	68(4)	29(3)	4(3)	9(3)
C(5)	48(3)	57(4)	69(4)	15(3)	-11(3)	9(3)
C(6)	87(6)	123(8)	103(6)	40(6)	-13(6)	51(6)
C(7)	48(4)	90(6)	180(9)	-27(6)	-25(5)	9(4)
C(8)	73(5)	79(5)	92(6)	5(5)	-4(5)	23(4)
C(11)	46(3)	68(4)	47(3)	-12(4)	4(2)	-16(4)
C(12)	48(3)	48(3)	74(4)	-4(3)	1(3)	8(3)
C(23)	38(3)	44(3)	63(3)	-1(3)	3(3)	-5(2)
C(24)	42(3)	67(4)	61(4)	-3(3)	-7(3)	-7(3)
C(31)	83(6)	121(8)	143(8)	-68(7)	19(6)	-52(6)
C(32)	94(6)	88(6)	135(8)	44(6)	-36(7)	-9(5)
C(33)	121(9)	171(11)	164(11)	98(9)	73(9)	50(9)
C(41)	90(6)	78(4)	45(3)	-6(3)	8(4)	-27(4)
C(42)	73(5)	58(4)	53(4)	-6(3)	18(4)	8(4)
C(43)	47(3)	92(5)	45(3)	10(4)	11(3)	-7(4)
C(44)	102(6)	49(4)	56(4)	6(3)	30(4)	-16(4)
C(45)	61(4)	88(5)	42(3)	22(4)	6(3)	14(4)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(4a)	1217	-1331	2153	77
H(4b)	907	-2088	1527	77
H(6a)	3048	-2315	2668	105
H(6b)	4444	-2569	2194	105
H(6c)	2951	-3014	1976	105
H(7a)	4920	-953	1736	87
H(7b)	3595	-726	2274	87
H(7c)	3668	-321	1430	87
H(8a)	3260	-1596	344	85
H(8b)	2897	-2585	645	85
H(8c)	4420	-2151	817	85
H(31a)	3286	2254	1171	60
H(31b)	4295	1778	1784	60
H(31c)	2959	2356	2062	60
H(32a)	875	305	3021	60
H(32b)	136	1268	3097	60
H(32c)	1780	1197	2871	60
H(33a)	28	3210	676	60
H(33b)	734	3011	1489	60
H(33c)	-921	3248	1433	60
H(41)	-1002	-744	-1088	71
H(42)	1459	-1204	-676	75
H(43)	2829	209	-242	64
H(44)	1134	1586	-447	59
H(45)	-1247	954	-970	71

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	3246(1)	5788(1)	2636(1)	46(1)*
Mo(2)	3266(1)	863(1)	2597(1)	42(1)*
P(1)	1977(3)	6722(1)	2948(2)	68(1)*
P(2)	1070(3)	5312(1)	2040(2)	70(1)*
P(3)	2212(3)	1621(1)	3269(2)	62(1)*
P(4)	969(3)	527(1)	1844(2)	55(1)*
F(7a)	5862(8)	6989(3)	2926(4)	111(4)*
F(8a)	7677(8)	7247(3)	3918(4)	109(4)*
F(9a)	7889(8)	6376(3)	3286(4)	111(4)*
F(10a)	8634(8)	6532(4)	5223(4)	125(4)*
F(11a)	8592(8)	5617(4)	4636(4)	128(4)*
F(12a)	7327(8)	5823(4)	5347(4)	131(4)*
F(1a)	6417(11)	4718(4)	1746(5)	150(6)*
F(2a)	5478(9)	3856(3)	1267(5)	144(6)*
F(3a)	4117(11)	4728(4)	1185(4)	136(5)*
F(4a)	7768(8)	4048(4)	3167(7)	182(6)*
F(5a)	6706(9)	3223(3)	2657(6)	158(6)*
F(6a)	6477(10)	3666(4)	3677(5)	150(5)*
F(1b)	8093(8)	1286(3)	3458(4)	114(4)*
F(2b)	7948(8)	2025(3)	4284(4)	108(4)*
F(3b)	6159(7)	1916(3)	3209(4)	106(4)*
F(4b)	8861(7)	1050(4)	5350(4)	118(4)*
F(5b)	8581(7)	291(4)	4484(4)	125(4)*
F(6b)	7419(8)	340(4)	5250(4)	133(4)*
F(7b)	5100(9)	-793(4)	730(5)	133(5)*
F(8b)	6259(10)	-46(4)	1443(5)	144(6)*
F(9b)	3960(11)	87(4)	896(4)	139(5)*
F(10b)	6253(9)	-1652(3)	1925(6)	155(6)*
F(11b)	7441(8)	-942(4)	2684(6)	164(6)*
F(12b)	6045(10)	-1409(4)	3034(5)	153(6)*
O(1a)	3001(9)	7301(3)	3257(5)	93(4)*
O(2a)	611(10)	7104(4)	2241(6)	137(6)*
O(3a)	1305(12)	6694(5)	3603(6)	140(7)*
O(4a)	1361(8)	4552(4)	1827(6)	119(5)*
O(5a)	-146(9)	5280(4)	2318(6)	117(5)*
O(6a)	-67(10)	5612(5)	1184(6)	146(6)*
O(7a)	5635(8)	6817(3)	4410(4)	84(2)
O(8a)	4012(8)	3883(4)	2310(4)	86(2)
O(1b)	3243(8)	2167(3)	3818(4)	85(4)*
O(2b)	1924(9)	1300(4)	3988(4)	98(5)*
O(3b)	785(10)	2088(4)	2784(7)	146(6)*
O(4b)	1136(8)	-163(4)	1434(5)	93(4)*
O(5b)	-107(8)	964(4)	1085(4)	96(4)*
O(6b)	-229(7)	407(3)	2222(4)	76(4)*
O(7b)	5909(8)	1500(3)	4663(4)	74(2)
O(8b)	3651(8)	-935(4)	1749(4)	88(2)
C(1a)	2582(16)	7979(6)	3283(8)	141(9)*
C(2a)	-702(16)	7251(10)	2097(9)	202(13)*
C(3a)	1766(19)	6721(11)	4367(8)	243(16)*
C(4a)	249(15)	4129(7)	1501(11)	186(12)*
C(5a)	361(15)	5056(7)	3220(7)	125(8)*
C(6a)	-1544(16)	5648(9)	862(11)	241(14)*
C(7a)	2755(10)	6144(4)	1675(5)	54(3)
C(8a)	2233(12)	6376(5)	815(6)	78(3)
C(9a)	3134(12)	6850(5)	618(6)	67(3)
C(10a)	4719(15)	6555(6)	857(8)	107(4)
C(11a)	2385(13)	7023(5)	-307(7)	90(4)
C(12a)	2937(17)	7481(7)	1094(9)	129(5)
C(21a)	6453(11)	6360(5)	4089(6)	60(3)
C(22a)	6993(12)	6750(5)	3572(6)	69(3)
C(1b)	3378(15)	2762(5)	3516(8)	116(8)*
C(2b)	1893(15)	1573(7)	4700(7)	120(9)*
C(3b)	-359(17)	2272(10)	2604(16)	325(21)*
C(4b)	-82(14)	-535(7)	980(9)	142(9)*
C(5b)	-1614(15)	1060(9)	783(10)	191(12)*
C(6b)	217(12)	30(5)	2945(6)	85(6)*
C(23a)	7790(13)	6077(5)	4824(7)	88(4)
C(18a)	5204(11)	4260(5)	2457(6)	65(3)
C(19a)	5306(13)	4384(5)	1670(7)	88(4)
C(20a)	6569(15)	3800(6)	2974(8)	104(4)
C(13a)	5759(10)	5429(4)	3022(5)	49(3)
C(14a)	5068(10)	4847(4)	2957(6)	52(3)
C(15a)	4539(10)	4879(4)	3594(5)	56(3)
C(16a)	4830(11)	5442(4)	4011(6)	60(3)
C(17a)	5606(11)	5803(4)	3668(5)	51(3)
C(13b)	5715(10)	431(4)	2886(5)	50(3)
C(17b)	4885(10)	-120(4)	2644(5)	51(3)
C(16b)	4360(10)	-209(4)	3259(5)	50(3)
C(15b)	4793(10)	242(4)	3835(6)	52(3)
C(14b)	5651(10)	663(4)	3618(5)	45(3)
C(18b)	6595(11)	1120(5)	4207(6)	58(3)
C(19b)	7221(12)	1581(5)	3804(7)	78(3)
C(20b)	7871(13)	696(5)	4844(7)	85(4)
C(21b)	4941(12)	-609(5)	2015(6)	71(3)
C(22b)	5051(14)	-352(6)	1300(7)	95(4)
C(23b)	6203(15)	-1158(7)	2421(8)	109(4)
C(7b)	2889(10)	1513(4)	1908(5)	55(3)
C(8b)	2514(13)	2132(5)	1388(6)	82(3)
C(9b)	3051(11)	2100(5)	695(6)	60(3)
C(10b)	2629(14)	2797(6)	270(7)	97(4)
C(11b)	2235(15)	1600(6)	97(8)	109(5)
C(12b)	4729(15)	1909(6)	994(7)	101(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-P(1)	2.343(3)	Mo(1)-P(2)	2.347(3)
Mo(1)-C(7a)	1.773(10)	Mo(1)-C(13a)	2.356(9)
Mo(1)-C(14a)	2.412(9)	Mo(1)-C(15a)	2.474(9)
Mo(1)-C(16a)	2.461(9)	Mo(1)-C(17a)	2.390(8)
Mo(2)-P(3)	2.330(3)	Mo(2)-P(4)	2.354(3)
Mo(2)-C(13b)	2.354(10)	Mo(2)-C(17b)	2.414(9)
Mo(2)-C(16b)	2.474(9)	Mo(2)-C(15b)	2.472(8)
Mo(2)-C(14b)	2.393(8)	Mo(2)-C(7b)	1.766(9)
P(1)-O(1a)	1.615(8)	P(1)-O(2a)	1.612(8)
P(1)-O(3a)	1.563(13)	P(2)-O(4a)	1.619(8)
P(2)-O(5a)	1.600(12)	P(2)-O(6a)	1.623(9)
P(3)-O(1b)	1.660(8)	P(3)-O(2b)	1.605(10)
P(3)-O(3b)	1.582(9)	P(4)-O(4b)	1.602(8)
P(4)-O(5b)	1.605(7)	P(4)-O(6b)	1.622(9)
F(7a)-C(22a)	1.337(11)	F(8a)-C(22a)	1.310(12)
F(9a)-C(22a)	1.342(15)	F(10a)-C(23a)	1.342(14)
F(11a)-C(23a)	1.282(15)	F(12a)-C(23a)	1.338(17)
F(1a)-C(19a)	1.334(17)	F(2a)-C(19a)	1.318(14)
F(3a)-C(19a)	1.314(13)	F(4a)-C(20a)	1.277(17)
F(5a)-C(20a)	1.317(15)	F(6a)-C(20a)	1.344(18)
F(1b)-C(19b)	1.327(16)	F(2b)-C(19b)	1.323(12)
F(3b)-C(19b)	1.329(11)	F(4b)-C(20b)	1.340(13)
F(5b)-C(20b)	1.334(15)	F(6b)-C(20b)	1.280(17)
F(7b)-C(22b)	1.361(15)	F(8b)-C(22b)	1.360(17)
F(9b)-C(22b)	1.318(13)	F(10b)-C(23b)	1.340(17)
F(11b)-C(23b)	1.274(17)	F(12b)-C(23b)	1.304(19)
O(1a)-C(1a)	1.414(14)	O(2a)-C(2a)	1.231(18)
O(3a)-C(3a)	1.279(17)	O(4a)-C(4a)	1.432(14)
O(5a)-C(5a)	1.414(16)	O(6a)-C(6a)	1.355(17)
O(7a)-C(21a)	1.418(14)	O(8a)-C(18a)	1.434(14)
O(1b)-C(1b)	1.400(15)	O(2b)-C(2b)	1.393(16)
O(3b)-C(3b)	1.080(19)	O(4b)-C(4b)	1.473(15)
O(5b)-C(5b)	1.379(16)	O(6b)-C(6b)	1.433(13)
O(7b)-C(18b)	1.413(14)	O(8b)-C(21b)	1.434(14)
C(7a)-C(8a)	1.512(14)	C(8a)-C(9a)	1.536(18)
C(9a)-C(10a)	1.521(18)	C(9a)-C(11a)	1.585(15)
C(9a)-C(12a)	1.569(19)	C(21a)-C(22a)	1.526(18)
C(21a)-C(23a)	1.552(13)	C(21a)-C(17a)	1.520(13)
C(18a)-C(19a)	1.492(18)	C(18a)-C(20a)	1.553(15)
C(18a)-C(14a)	1.508(14)	C(13a)-C(14a)	1.437(14)
C(13a)-C(17a)	1.418(14)	C(14a)-C(15a)	1.426(16)
C(15a)-C(16a)	1.363(13)	C(16a)-C(17a)	1.436(17)
C(13b)-C(17b)	1.446(13)	C(13b)-C(14b)	1.408(14)
C(17b)-C(16b)	1.415(16)	C(17b)-C(21b)	1.505(15)
C(16b)-C(15b)	1.352(12)	C(15b)-C(14b)	1.446(15)
C(14b)-C(18b)	1.518(12)	C(18b)-C(19b)	1.532(18)
C(18b)-C(20b)	1.549(13)	C(21b)-C(22b)	1.456(19)
C(21b)-C(23b)	1.553(16)	C(7b)-C(8b)	1.533(14)
C(8b)-C(9b)	1.528(18)	C(9b)-C(10b)	1.586(15)
C(9b)-C(11b)	1.536(16)	C(9b)-C(12b)	1.552(17)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic thermal parameters ($Å^2x10^3$)

	x	y	z	U
H(1aa)	3433	8205	3488	117
H(1ab)	2036	8052	3626	117
H(1ac)	1983	8139	2754	117
H(2aa)	-1157	7493	1603	195
H(2ab)	-819	7512	2525	195
H(2ac)	-1152	6859	2060	195
H(3aa)	975	6700	4546	211
H(3ab)	2181	7121	4540	211
H(3ac)	2501	6358	4587	211
H(4aa)	689	3704	1424	164
H(4ab)	-439	4303	996	164
H(4ac)	-248	4093	1861	164
H(5aa)	-450	5054	3387	114
H(5ab)	1026	5340	3558	114
H(5ac)	856	4622	3260	114
H(6aa)	-1892	5782	311	208
H(6ab)	-1950	5961	1152	208
H(6ac)	-1837	5228	899	208
H(8aa)	2224	5997	490	84
H(8ab)	1255	6590	674	84
H(1ba)	4021	2998	3942	103
H(1bb)	2437	3015	3295	103
H(1bc)	3776	2681	3106	103
H(2ba)	1694	1252	5006	115
H(2bb)	1142	1937	4581	115
H(2bc)	2822	1719	5003	115
H(3ba)	-708	2453	2073	296
H(3bb)	-475	2605	2967	296
H(3bc)	-908	1923	2613	296
H(4ba)	291	-928	786	126
H(4bb)	-764	-276	535	126
H(4bc)	-566	-645	1323	126
H(5ba)	-1954	1352	330	170
H(5bb)	-1950	1244	1188	170
H(5bc)	-1986	649	620	170
H(6ba)	-608	9	3095	84
H(6bb)	958	229	3365	84
H(6bc)	600	-403	2857	84
H(13a)	6241	5548	2683	49
H(15a)	4045	4548	3712	64
H(16a)	4565	5573	4460	68
H(13b)	6226	608	2596	57
H(16b)	3774	-544	3265	51
H(15b)	4566	277	4310	57
H(8ba)	1470	2231	1170	86
H(8bb)	2938	2479	1730	86

(XI)

Table 3. Bond angles (°)

P(1)-Mo(1)-P(2)	91.0(1)	P(1)-Mo(1)-C(7a)	87.0(3)
P(2)-Mo(1)-C(7a)	84.1(3)	P(1)-Mo(1)-C(13a)	132.2(2)
P(2)-Mo(1)-C(13a)	135.8(2)	C(7a)-Mo(1)-C(13a)	104.1(4)
P(1)-Mo(1)-C(14a)	154.2(2)	P(2)-Mo(1)-C(14a)	102.1(2)
C(7a)-Mo(1)-C(14a)	116.2(4)	C(13a)-Mo(1)-C(14a)	35.1(3)
P(1)-Mo(1)-C(15a)	123.6(3)	P(2)-Mo(1)-C(15a)	95.4(2)
C(7a)-Mo(1)-C(15a)	149.4(4)	C(13a)-Mo(1)-C(15a)	56.1(4)
C(14a)-Mo(1)-C(15a)	33.9(4)	P(1)-Mo(1)-C(16a)	97.9(3)
P(2)-Mo(1)-C(16a)	117.6(3)	C(7a)-Mo(1)-C(16a)	157.5(4)
C(13a)-Mo(1)-C(16a)	56.7(4)	C(14a)-Mo(1)-C(16a)	56.3(3)
C(15a)-Mo(1)-C(16a)	32.1(3)	P(1)-Mo(1)-C(17a)	100.7(2)
P(2)-Mo(1)-C(17a)	150.5(3)	C(7a)-Mo(1)-C(17a)	123.2(4)
C(13a)-Mo(1)-C(17a)	34.8(3)	C(14a)-Mo(1)-C(17a)	57.9(3)
C(15a)-Mo(1)-C(17a)	55.6(3)	C(16a)-Mo(1)-C(17a)	34.4(4)
P(3)-Mo(2)-P(4)	90.9(1)	P(3)-Mo(2)-C(13b)	131.3(2)
P(4)-Mo(2)-C(13b)	135.4(2)	P(3)-Mo(2)-C(17b)	148.7(2)
P(4)-Mo(2)-C(17b)	101.7(2)	C(13b)-Mo(2)-C(17b)	35.3(3)
P(3)-Mo(2)-C(16b)	117.5(3)	P(4)-Mo(2)-C(16b)	95.4(2)
C(13b)-Mo(2)-C(16b)	56.2(4)	C(17b)-Mo(2)-C(16b)	33.6(4)
P(3)-Mo(2)-C(15b)	93.2(2)	P(4)-Mo(2)-C(15b)	117.7(2)
C(13b)-Mo(2)-C(15b)	56.4(4)	C(17b)-Mo(2)-C(15b)	55.6(3)
C(16b)-Mo(2)-C(15b)	31.7(3)	P(3)-Mo(2)-C(14b)	98.5(2)
P(4)-Mo(2)-C(14b)	150.7(2)	C(13b)-Mo(2)-C(14b)	34.5(3)
C(17b)-Mo(2)-C(14b)	57.7(3)	C(16b)-Mo(2)-C(14b)	55.7(3)
C(15b)-Mo(2)-C(14b)	34.5(3)	P(3)-Mo(2)-C(7b)	83.9(3)
P(4)-Mo(2)-C(7b)	89.3(3)	C(13b)-Mo(2)-C(7b)	106.4(4)
C(17b)-Mo(2)-C(7b)	124.3(4)	C(16b)-Mo(2)-C(7b)	157.9(4)
C(15b)-Mo(2)-C(7b)	152.9(4)	C(14b)-Mo(2)-C(7b)	119.2(4)
Mo(1)-P(1)-O(1a)	111.4(3)	Mo(1)-P(1)-O(2a)	118.9(4)
O(1a)-P(1)-O(2a)	99.9(4)	Mo(1)-P(1)-O(3a)	120.7(4)
O(1a)-P(1)-O(3a)	102.6(5)	O(2a)-P(1)-O(3a)	100.3(6)
Mo(1)-P(2)-O(4a)	112.3(3)	Mo(1)-P(2)-O(5a)	125.7(3)
O(4a)-P(2)-O(5a)	101.0(5)	Mo(1)-P(2)-O(6a)	117.1(4)
O(4a)-P(2)-O(6a)	101.8(5)	O(5a)-P(2)-O(6a)	95.2(5)
Mo(2)-P(3)-O(1b)	117.2(4)	Mo(2)-P(3)-O(2b)	112.9(3)
O(1b)-P(3)-O(2b)	96.4(4)	Mo(2)-P(3)-O(3b)	120.0(5)
O(1b)-P(3)-O(3b)	99.7(4)	O(2b)-P(3)-O(3b)	107.3(6)
Mo(2)-P(4)-O(4b)	111.3(3)	Mo(2)-P(4)-O(5b)	118.6(3)
O(4b)-P(4)-O(5b)	101.3(4)	Mo(2)-P(4)-O(6b)	123.6(3)
O(4b)-P(4)-O(6b)	100.8(4)	O(5b)-P(4)-O(6b)	97.7(4)
P(1)-O(1a)-C(1a)	128.7(8)	P(1)-O(2a)-C(2a)	136.1(12)
P(1)-O(3a)-C(3a)	136.4(12)	P(2)-O(4a)-C(4a)	124.7(8)
P(2)-O(5a)-C(5a)	116.4(8)	P(2)-O(6a)-C(6a)	129.6(12)
P(3)-O(1b)-C(1b)	123.9(7)	P(3)-O(2b)-C(2b)	129.9(8)
P(3)-O(3b)-C(3b)	154.2(17)	P(4)-O(4b)-C(4b)	125.0(8)
P(4)-O(5b)-C(5b)	128.4(10)	P(4)-O(6b)-C(6b)	119.6(7)
Mo(1)-C(7a)-C(8a)	172.8(8)	C(7a)-C(8a)-C(9a)	116.8(8)
C(8a)-C(9a)-C(10a)	110.8(9)	C(8a)-C(9a)-C(11a)	107.8(8)
C(10a)-C(9a)-C(11a)	112.5(11)	C(8a)-C(9a)-C(12a)	104.2(11)
C(10a)-C(9a)-C(12a)	113.2(9)	C(11a)-C(9a)-C(12a)	107.9(9)
O(7a)-C(21a)-C(22a)	106.6(8)	O(7a)-C(21a)-C(23a)	105.0(8)
C(22a)-C(21a)-C(23a)	108.6(9)	O(7a)-C(21a)-C(17a)	112.5(9)
C(22a)-C(21a)-C(17a)	115.1(9)	C(23a)-C(21a)-C(17a)	108.5(8)
F(7a)-C(22a)-F(8a)	106.4(8)	F(7a)-C(22a)-F(9a)	105.3(9)
F(8a)-C(22a)-F(9a)	106.7(10)	F(7a)-C(22a)-C(21a)	109.8(9)
F(8a)-C(22a)-C(21a)	115.7(9)	F(9a)-C(22a)-C(21a)	112.3(8)
F(10a)-C(23a)-F(11a)	108.5(10)	F(10a)-C(23a)-F(12a)	106.1(10)
F(11a)-C(23a)-F(12a)	106.9(10)	F(10a)-C(23a)-C(21a)	112.9(9)
F(11a)-C(23a)-C(21a)	112.6(10)	F(12a)-C(23a)-C(21a)	109.5(10)
O(8a)-C(18a)-C(19a)	107.5(8)	O(8a)-C(18a)-C(20a)	104.1(9)
C(19a)-C(18a)-C(20a)	109.3(11)	O(8a)-C(18a)-C(14a)	110.7(10)
C(19a)-C(18a)-C(14a)	117.2(9)	C(20a)-C(18a)-C(14a)	107.3(8)
F(1a)-C(19a)-F(2a)	105.9(12)	F(1a)-C(19a)-F(3a)	106.5(10)
F(2a)-C(19a)-F(3a)	105.0(9)	F(1a)-C(19a)-C(18a)	112.1(9)
F(2a)-C(19a)-C(18a)	115.0(10)	F(3a)-C(19a)-C(18a)	111.6(11)
F(4a)-C(20a)-F(5a)	109.2(12)	F(4a)-C(20a)-F(6a)	104.3(10)
F(5a)-C(20a)-F(6a)	104.3(11)	F(4a)-C(20a)-C(18a)	114.0(11)
F(5a)-C(20a)-C(18a)	114.0(9)	F(6a)-C(20a)-C(18a)	110.2(12)
Mo(1)-C(13a)-C(14a)	74.6(5)	Mo(1)-C(13a)-C(17a)	74.0(5)
C(14a)-C(13a)-C(17a)	108.9(10)	Mo(1)-C(14a)-C(18a)	129.6(6)
Mo(1)-C(14a)-C(13a)	70.3(5)	C(18a)-C(14a)-C(13a)	126.4(11)
Mo(1)-C(14a)-C(15a)	75.4(5)	C(18a)-C(14a)-C(15a)	127.0(9)
C(13a)-C(14a)-C(15a)	105.1(8)	Mo(1)-C(15a)-C(14a)	70.7(5)
Mo(1)-C(15a)-C(16a)	73.5(5)	C(14a)-C(15a)-C(16a)	110.9(10)
Mo(1)-C(16a)-C(15a)	74.5(5)	Mo(1)-C(16a)-C(17a)	70.1(5)
C(15a)-C(16a)-C(17a)	108.3(10)	Mo(1)-C(17a)-C(21a)	132.0(6)
Mo(1)-C(17a)-C(13a)	71.3(5)	C(21a)-C(17a)-C(13a)	127.5(10)
Mo(1)-C(17a)-C(16a)	75.5(5)	C(21a)-C(17a)-C(16a)	123.4(9)
C(13a)-C(17a)-C(16a)	106.7(8)	Mo(2)-C(13b)-C(17b)	74.6(5)
Mo(2)-C(13b)-C(14b)	74.2(6)	C(17b)-C(13b)-C(14b)	108.7(10)
Mo(2)-C(17b)-C(13b)	70.1(5)	Mo(2)-C(17b)-C(16b)	75.5(5)
C(13b)-C(17b)-C(16b)	105.4(8)	Mo(2)-C(17b)-C(21b)	132.1(6)
C(13b)-C(17b)-C(21b)	126.5(11)	C(16b)-C(17b)-C(21b)	125.9(9)
Mo(2)-C(16b)-C(17b)	70.9(5)	Mo(2)-C(16b)-C(15b)	74.1(5)
C(17b)-C(16b)-C(15b)	110.9(9)	Mo(2)-C(15b)-C(16b)	74.2(5)
Mo(2)-C(15b)-C(14b)	69.7(5)	C(16b)-C(15b)-C(14b)	108.6(10)
Mo(2)-C(14b)-C(13b)	71.3(5)	Mo(2)-C(14b)-C(15b)	75.8(5)
C(13b)-C(14b)-C(15b)	106.3(8)	Mo(2)-C(14b)-C(18b)	131.0(6)
C(13b)-C(14b)-C(18b)	129.0(10)	C(15b)-C(14b)-C(18b)	122.6(9)
O(7b)-C(18b)-C(14b)	115.2(9)	O(7b)-C(18b)-C(19b)	108.2(8)
C(14b)-C(18b)-C(19b)	112.5(9)	O(7b)-C(18b)-C(20b)	103.6(8)
C(14b)-C(18b)-C(20b)	107.8(8)	C(19b)-C(18b)-C(20b)	109.1(9)
F(1b)-C(19b)-F(2b)	106.8(10)	F(1b)-C(19b)-F(3b)	103.8(9)
F(2b)-C(19b)-F(3b)	105.5(8)	F(1b)-C(19b)-C(18b)	114.7(9)
F(2b)-C(19b)-C(18b)	114.4(10)	F(3b)-C(19b)-C(18b)	110.8(9)
F(4b)-C(20b)-F(5b)	106.5(10)	F(4b)-C(20b)-F(6b)	108.8(9)
F(5b)-C(20b)-F(6b)	106.8(9)	F(4b)-C(20b)-C(18b)	112.9(9)
F(5b)-C(20b)-C(18b)	109.6(9)	F(6b)-C(20b)-C(18b)	112.0(10)
O(8b)-C(21b)-C(17b)	109.8(10)	O(8b)-C(21b)-C(22b)	106.4(8)
C(17b)-C(21b)-C(22b)	116.2(9)	O(8b)-C(21b)-C(23b)	104.2(9)
C(17b)-C(21b)-C(23b)	108.0(8)	C(22b)-C(21b)-C(23b)	111.5(11)
F(7b)-C(22b)-F(8b)	103.3(12)	F(7b)-C(22b)-F(9b)	102.8(9)
F(8b)-C(22b)-F(9b)	103.9(10)	F(7b)-C(22b)-C(21b)	116.4(10)
F(8b)-C(22b)-C(21b)	114.2(9)	F(9b)-C(22b)-C(21b)	114.7(12)
F(10b)-C(23b)-F(11b)	108.3(13)	F(10b)-C(23b)-F(12b)	106.7(12)
F(11b)-C(23b)-F(12b)	106.6(11)	F(10b)-C(23b)-C(21b)	112.5(9)
F(11b)-C(23b)-C(21b)	111.6(11)	F(12b)-C(23b)-C(21b)	110.8(13)
Mo(2)-C(7b)-C(8b)	172.8(8)	C(7b)-C(8b)-C(9b)	116.3(9)
C(8b)-C(9b)-C(10b)	108.0(9)	C(8b)-C(9b)-C(11b)	107.6(10)
C(10b)-C(9b)-C(11b)	108.7(8)	C(8b)-C(9b)-C(12b)	111.2(8)
C(10b)-C(9b)-C(12b)	110.0(10)	C(11b)-C(9b)-C(12b)	111.2(9)

(XI)

Table 4. Anisotropic thermal parameters ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	45(1)	46(1)	48(1)	4(1)	20(1)	-4(1)
Mo(2)	40(1)	42(1)	45(1)	2(1)	16(1)	-5(1)
P(1)	63(2)	67(2)	79(2)	-7(2)	35(2)	-1(2)
P(2)	55(2)	71(2)	84(2)	-1(2)	24(2)	-13(2)
P(3)	51(2)	52(2)	85(2)	-12(2)	30(2)	-8(1)
P(4)	45(2)	67(2)	51(2)	-4(1)	15(1)	-9(1)
F(7a)	112(6)	109(5)	94(5)	38(4)	6(4)	-40(5)
F(8a)	115(6)	81(5)	123(6)	-33(4)	27(5)	-52(4)
F(9a)	132(7)	100(5)	146(6)	-27(5)	95(6)	-45(5)
F(10a)	91(6)	152(7)	95(5)	-30(5)	-10(4)	-27(5)
F(11a)	95(6)	127(6)	121(6)	-1(5)	7(5)	35(5)
F(12a)	108(6)	191(8)	77(5)	42(5)	10(5)	-17(6)
F(1a)	222(10)	136(7)	186(8)	-84(6)	164(8)	-107(7)
F(2a)	174(8)	92(5)	227(9)	-89(6)	140(7)	-47(5)
F(3a)	198(10)	127(6)	88(5)	-12(5)	71(6)	15(6)
F(4a)	56(5)	90(6)	356(14)	27(7)	25(7)	-4(4)
F(5a)	122(7)	61(5)	280(11)	-19(6)	70(7)	6(5)
F(6a)	141(8)	95(6)	177(8)	47(6)	30(6)	44(5)
F(1b)	122(7)	118(6)	146(6)	-49(5)	88(5)	-72(5)
F(2b)	103(6)	101(5)	117(6)	-47(4)	28(5)	-63(4)
F(3b)	111(6)	89(5)	106(5)	25(4)	15(4)	-51(4)
F(4b)	70(5)	159(7)	88(5)	-19(5)	-13(4)	-23(5)
F(5b)	65(5)	149(7)	113(6)	-5(5)	-8(4)	30(5)
F(6b)	97(6)	178(8)	87(5)	68(5)	-16(5)	-29(5)
F(7b)	134(7)	129(6)	143(7)	-86(5)	67(6)	-19(5)
F(8b)	174(9)	178(8)	139(7)	-70(6)	110(7)	-94(7)
F(9b)	208(10)	120(6)	101(6)	-2(5)	85(6)	21(6)
F(10b)	112(7)	68(5)	277(11)	-74(6)	76(7)	4(4)
F(11b)	53(5)	103(6)	290(12)	-47(7)	21(6)	9(4)
F(12b)	157(9)	86(5)	190(9)	19(6)	55(7)	58(6)
O(1a)	90(6)	61(5)	134(7)	-35(5)	52(6)	-7(4)
O(2a)	84(7)	121(7)	174(10)	37(7)	27(7)	53(6)
O(3a)	166(10)	151(9)	152(9)	-53(7)	109(8)	-50(7)
O(4a)	62(6)	84(6)	200(10)	-52(6)	34(6)	-25(5)
O(5a)	91(7)	130(7)	152(9)	-24(6)	58(6)	-53(6)
O(6a)	90(8)	181(10)	133(8)	44(7)	-11(6)	-54(7)
O(1b)	93(6)	72(5)	103(6)	-26(4)	49(5)	-27(4)
O(2b)	129(8)	110(6)	91(6)	-36(5)	76(6)	-43(6)
O(3b)	74(7)	115(7)	222(12)	2(7)	43(7)	49(6)
O(4b)	57(5)	99(6)	121(7)	-61(5)	28(5)	-32(5)
O(5b)	52(5)	149(7)	64(5)	20(5)	-7(4)	-18(5)
O(6b)	49(5)	102(6)	79(5)	-3(4)	22(4)	-19(4)
C(1a)	144(14)	102(11)	150(13)	-39(10)	25(11)	-15(10)
C(2a)	107(15)	354(27)	115(14)	58(16)	22(12)	36(16)
C(3a)	145(18)	509(37)	85(13)	2(18)	29(12)	-113(21)
C(4a)	81(11)	113(12)	343(25)	-107(14)	51(14)	-53(10)
C(5a)	110(12)	162(13)	96(11)	39(9)	19(9)	-41(10)
C(6a)	102(14)	246(22)	276(24)	145(19)	-64(15)	-54(14)
C(1b)	145(14)	81(9)	138(12)	9(9)	65(11)	-31(9)
C(2b)	151(14)	155(12)	85(10)	-33(9)	68(10)	-62(11)
C(3b)	102(15)	300(26)	590(45)	318(30)	159(22)	97(16)
C(4b)	76(11)	143(13)	196(16)	-79(12)	29(11)	-59(10)
C(5b)	94(13)	240(20)	196(18)	131(16)	9(13)	27(13)
C(6b)	87(10)	94(9)	79(8)	20(7)	27(7)	-35(7)

The anisotropic temperature factor exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo	1659(1)	795(1)	2043(1)	13(1)*
I	1355(1)	-1132(1)	1586(1)	20(1)*
P(1)	346(1)	404(1)	3064(1)	17(1)*
P(2)	3834(1)	671(1)	1706(1)	16(1)*
O(1)	572(3)	-538(2)	3604(2)	25(1)*
O(2)	423(3)	1239(2)	3711(2)	24(1)*
O(3)	-1246(3)	321(2)	2775(2)	23(1)*
O(4)	3986(3)	682(2)	754(2)	21(1)*
O(5)	4696(3)	1581(2)	2015(2)	21(1)*
O(6)	4803(3)	-202(2)	1991(2)	22(1)*
C(1)	1823(4)	-958(3)	3949(3)	25(1)*
C(2)	-336(5)	1239(4)	4349(3)	34(2)*
C(3)	-1806(4)	-425(3)	2223(3)	29(1)*
C(4)	3389(5)	-45(3)	198(3)	29(1)*
C(5)	6062(4)	1671(3)	1963(3)	30(1)*
C(6)	4940(4)	-706(3)	2757(3)	25(1)*
C(7)	2907(4)	897(3)	3090(2)	17(1)*
C(8)	3755(4)	994(3)	3816(2)	19(1)*
C(9)	4160(4)	1887(3)	4307(3)	23(1)*
C(10)	3956(6)	1743(4)	5184(3)	38(2)*
C(11)	3335(5)	2718(3)	3903(3)	33(1)*
C(12)	5633(5)	2077(4)	4340(4)	43(2)*
C(13)	1352(4)	1705(3)	821(2)	23(1)*
C(14)	120(4)	1279(3)	776(3)	27(1)*
C(15)	-361(4)	1552(3)	1471(3)	27(1)*
C(16)	575(4)	2165(3)	1969(3)	22(1)*
C(17)	1657(4)	2268(3)	1563(2)	20(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo-I	2.856(1)	Mo-P(1)	2.457(1)
Mo-P(2)	2.444(1)	Mo-C(7)	1.927(3)
Mo-C(13)	2.370(4)	Mo-C(14)	2.441(4)
Mo-C(15)	2.362(4)	Mo-C(16)	2.246(4)
Mo-C(17)	2.251(4)	P(1)-O(1)	1.606(3)
P(1)-O(2)	1.595(3)	P(1)-O(3)	1.618(3)
P(2)-O(4)	1.621(3)	P(2)-O(5)	1.598(3)
P(2)-O(6)	1.606(3)	O(1)-C(1)	1.429(5)
O(2)-C(2)	1.450(7)	O(3)-C(3)	1.441(5)
O(4)-C(4)	1.436(5)	O(5)-C(5)	1.442(5)
O(6)-C(6)	1.440(5)	C(7)-C(8)	1.333(5)
C(8)-C(9)	1.523(6)	C(8)-H(8)	0.936(46)
C(9)-C(10)	1.527(7)	C(9)-C(11)	1.529(6)
C(9)-C(12)	1.540(7)	C(13)-C(14)	1.402(6)
C(13)-C(17)	1.446(6)	C(14)-C(15)	1.406(7)
C(15)-C(16)	1.427(6)	C(16)-C(17)	1.436(6)

Table 3. Bond angles (°)

I-Mo-P(1)	85.3(1)	I-Mo-P(2)	85.6(1)
P(1)-Mo-P(2)	145.0(1)	I-Mo-C(7)	108.9(1)
P(1)-Mo-C(7)	76.2(1)	P(2)-Mo-C(7)	75.0(1)
I-Mo-C(13)	108.4(1)	P(1)-Mo-C(13)	136.3(1)
P(2)-Mo-C(13)	78.6(1)	C(7)-Mo-C(13)	131.7(2)
I-Mo-C(14)	91.8(1)	P(1)-Mo-C(14)	107.5(1)
P(2)-Mo-C(14)	106.5(1)	C(7)-Mo-C(14)	159.2(2)
C(13)-Mo-C(14)	33.8(1)	I-Mo-C(15)	107.4(1)
P(1)-Mo-C(15)	78.7(1)	P(2)-Mo-C(15)	136.2(1)
C(7)-Mo-C(15)	133.4(2)	C(13)-Mo-C(15)	57.6(2)
C(14)-Mo-C(15)	34.0(2)	I-Mo-C(16)	143.2(1)
P(1)-Mo-C(16)	83.7(1)	P(2)-Mo-C(16)	121.7(1)
C(7)-Mo-C(16)	102.3(1)	C(13)-Mo-C(16)	60.2(2)
C(14)-Mo-C(16)	58.8(1)	C(15)-Mo-C(16)	36.0(1)
I-Mo-C(17)	144.8(1)	P(1)-Mo-C(17)	119.9(1)
P(2)-Mo-C(17)	85.2(1)	C(7)-Mo-C(17)	101.3(1)
C(13)-Mo-C(17)	36.4(1)	C(14)-Mo-C(17)	58.7(1)
C(15)-Mo-C(17)	59.8(1)	C(16)-Mo-C(17)	37.2(2)
Mo-P(1)-O(1)	122.7(1)	Mo-P(1)-O(2)	109.9(1)
O(1)-P(1)-O(2)	105.8(2)	Mo-P(1)-O(3)	119.7(1)
O(1)-P(1)-O(3)	96.7(2)	O(2)-P(1)-O(3)	98.7(2)
Mo-P(2)-O(4)	121.0(1)	Mo-P(2)-O(5)	110.3(1)
O(4)-P(2)-O(5)	97.9(2)	Mo-P(2)-O(6)	122.5(1)
O(4)-P(2)-O(6)	96.1(2)	O(5)-P(2)-O(6)	105.6(1)
P(1)-O(1)-C(1)	125.7(3)	P(1)-O(2)-C(2)	122.4(3)
P(1)-O(3)-C(3)	119.0(3)	P(2)-O(4)-C(4)	119.8(3)
P(2)-O(5)-C(5)	122.7(3)	P(2)-O(6)-C(6)	125.6(3)
Mo-C(7)-C(8)	178.2(3)	C(7)-C(8)-C(9)	128.3(3)
C(7)-C(8)-H(8)	120.7(28)	C(9)-C(8)-H(8)	110.9(27)
C(8)-C(9)-C(10)	108.5(4)	C(8)-C(9)-C(11)	110.8(3)
C(8)-C(9)-C(12)	108.7(4)	Mo-C(13)-C(14)	75.9(3)
Mo-C(13)-C(17)	67.3(2)	C(14)-C(13)-C(17)	108.2(4)
Mo-C(14)-C(13)	70.3(2)	Mo-C(14)-C(15)	69.9(2)
C(13)-C(14)-C(15)	108.6(4)	Mo-C(15)-C(14)	76.1(2)
Mo-C(15)-C(16)	67.6(2)	C(14)-C(15)-C(16)	109.0(4)
Mo-C(16)-C(15)	76.4(2)	Mo-C(16)-C(17)	71.5(2)
C(15)-C(16)-C(17)	107.1(4)	Mo-C(17)-C(13)	76.3(2)
Mo-C(17)-C(16)	71.2(2)	C(13)-C(17)-C(16)	107.1(3)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	11(1)	13(1)	14(1)	0(1)	3(1)	0(1)
I	23(1)	16(1)	23(1)	-3(1)	7(1)	-3(1)
P(1)	14(1)	18(1)	21(1)	1(1)	7(1)	0(1)
P(2)	14(1)	17(1)	19(1)	2(1)	6(1)	1(1)
O(1)	22(1)	28(2)	27(1)	9(1)	11(1)	4(1)
O(2)	26(1)	25(2)	26(1)	-3(1)	14(1)	-1(1)
O(3)	15(1)	23(1)	31(1)	3(1)	8(1)	1(1)
O(4)	23(1)	21(1)	22(1)	-0(1)	9(1)	-1(1)
O(5)	12(1)	22(1)	29(1)	-1(1)	5(1)	-3(1)
O(6)	18(1)	23(1)	26(1)	6(1)	8(1)	4(1)
C(1)	23(2)	27(2)	26(2)	10(2)	7(2)	3(2)
C(2)	45(3)	34(2)	32(2)	0(2)	27(2)	3(2)
C(3)	17(2)	24(2)	45(3)	-2(2)	5(2)	-1(2)
C(4)	34(2)	27(2)	28(2)	-5(2)	11(2)	-5(2)
C(5)	12(2)	31(2)	47(3)	0(2)	10(2)	-3(2)
C(6)	25(2)	21(2)	32(2)	8(2)	10(2)	8(2)
C(7)	19(2)	13(2)	19(2)	1(1)	6(1)	1(1)
C(8)	18(2)	17(2)	20(2)	2(1)	2(1)	2(1)
C(9)	24(2)	19(2)	23(2)	1(2)	-1(2)	3(2)
C(10)	61(3)	31(2)	20(2)	-6(2)	6(2)	3(2)
C(11)	45(3)	18(2)	30(2)	-4(2)	-5(2)	5(2)
C(12)	27(2)	41(3)	54(3)	-8(2)	-8(2)	-8(2)
C(13)	26(2)	25(2)	20(2)	10(2)	5(1)	7(2)
C(14)	26(2)	22(2)	28(2)	7(2)	-6(2)	-0(2)
C(15)	12(2)	30(2)	38(2)	13(2)	3(2)	6(2)
C(16)	26(2)	20(2)	21(2)	5(1)	8(2)	9(2)
C(17)	19(2)	16(2)	25(2)	5(1)	4(1)	1(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

(XII)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
H(1a)	1611	-1551	4159	31
H(1b)	2286	-579	4398	31
H(1c)	2372	-1055	3559	31
H(2a)	-137	1781	4696	43
H(2b)	41	695	4651	43
H(2c)	-1277	1165	4181	43
H(3a)	-2737	-295	2110	35
H(3b)	-1640	-1022	2492	35
H(3c)	-1510	-437	1714	35
H(4a)	3640	-41	-326	35
H(4b)	2445	8	111	35
H(4c)	3674	-619	482	35
H(5a)	6300	2321	1996	35
H(5b)	6206	1413	1455	35
H(5c)	6596	1342	2422	35
H(6a)	5284	-1308	2654	30
H(6b)	4099	-784	2901	30
H(6c)	5544	-406	3204	30
H(10a)	4258	2286	5513	45
H(10b)	4494	1215	5400	45
H(10c)	3052	1618	5200	45
H(11a)	3424	2822	3346	39
H(11b)	3617	3266	4229	39
H(11c)	2426	2590	3904	39
H(12a)	5841	2614	4692	51
H(12b)	5708	2238	3790	51
H(12c)	6239	1580	4546	51
H(13)	1899	1634	427	28
H(14)	-326	871	343	32
H(15)	-1183	1356	1593	31
H(16)	495	2455	2478	28
H(17)	2436	2641	1751	25
H(8)	4150(45)	470(34)	4108(29)	21(12)

(XIV)

Table 1. Atomic coordinates ($x10^4$) and isotropic thermal parameters ($Å^2 x10^3$)

	x	y	z	U
Mo	2034(1)	2043(1)	3391(1)	34(1)*
Br	245(1)	681(1)	3053(1)	53(1)*
P(1)	334(2)	2541(1)	4206(1)	42(1)*
P(2)	3651(2)	804(1)	3237(1)	48(1)*
O(1)	366(5)	3583(3)	4451(3)	65(2)*
O(2)	329(4)	2117(3)	5082(3)	52(2)*
O(3)	-1258(4)	2480(3)	3745(3)	62(2)*
O(4a)	3703(8)	-105(4)	3687(5)	71(3)*
O(4b)	4163(18)	196(14)	4098(11)	39(6)
O(5)	5207(4)	1131(3)	3339(3)	65(2)*
O(6a)	3519(8)	454(5)	2294(4)	93(3)*
O(6b)	3280(17)	-94(10)	2734(8)	31(6)
C(1)	1280(8)	3937(5)	5122(5)	83(3)*
C(2)	423(8)	1170(4)	5238(4)	60(3)*
C(3)	-2376(8)	2660(6)	4167(6)	80(3)*
C(4)	3173(7)	-297(5)	4415(4)	66(3)*
C(5)	6339(8)	521(6)	3252(5)	82(3)*
C(6)	2811(14)	-269(8)	1915(6)	163(7)*
C(7)	3158(5)	1998(3)	4462(3)	37(2)*
C(8)	3970(6)	1988(4)	5194(4)	41(2)*
C(9)	5044(6)	2651(4)	5533(3)	39(2)*
C(10)	5966(7)	2480(4)	6273(4)	52(2)*
C(11)	7010(7)	3083(5)	6581(4)	64(3)*
C(12)	7162(7)	3879(4)	6183(4)	66(3)*
C(13)	6240(7)	4077(4)	5474(4)	61(3)*
C(14)	5201(6)	3467(4)	5150(4)	47(2)*
C(15)	1215(8)	2651(5)	2049(4)	66(3)*
C(16)	999(8)	3271(5)	2624(4)	66(3)*
C(17)	2326(8)	3511(4)	3107(4)	62(3)*
C(18)	3372(8)	3002(4)	2812(4)	66(3)*
C(19)	2668(8)	2481(5)	2147(4)	65(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

(XIV)

Table 2. Bond lengths (Å)

Mo-Br	2.651(1)	Mo-P(1)	2.462(2)
Mo-P(2)	2.463(2)	Mo-C(7)	1.917(5)
Mo-C(15)	2.417(7)	Mo-C(16)	2.338(7)
Mo-C(17)	2.250(7)	Mo-C(18)	2.271(8)
Mo-C(19)	2.386(7)	P(1)-O(1)	1.593(4)
P(1)-O(2)	1.604(5)	P(1)-O(3)	1.596(4)
P(2)-O(4a)	1.538(7)	P(2)-O(4b)	1.695(18)
P(2)-O(5)	1.569(5)	P(2)-O(6a)	1.650(7)
P(2)-O(6b)	1.578(14)	O(1)-C(1)	1.395(9)
O(2)-C(2)	1.424(7)	O(3)-C(3)	1.438(10)
O(4a)-O(4b)	0.870(19)	O(4a)-O(6b)	1.577(16)
O(4a)-C(4)	1.448(12)	O(4b)-C(4)	1.396(21)
O(5)-C(5)	1.454(9)	O(6a)-O(6b)	1.151(17)
O(6a)-C(6)	1.361(14)	O(6b)-C(6)	1.388(16)
C(7)-C(8)	1.327(7)	C(8)-H(8)	0.905(59)
C(8)-C(9)	1.465(8)	C(9)-C(10)	1.409(7)
C(9)-C(14)	1.390(8)	C(10)-C(11)	1.375(9)
C(11)-C(12)	1.377(10)	C(12)-C(13)	1.377(9)
C(13)-C(14)	1.385(8)	C(15)-C(16)	1.379(10)
C(15)-C(19)	1.416(11)	C(16)-C(17)	1.430(10)
C(17)-C(18)	1.433(11)	C(18)-C(19)	1.418(9)

Table 3. Bond angles (°)

Br-Mo-P(1)	82.0(1)	Br-Mo-P(2)	79.7(1)
P(1)-Mo-P(2)	142.7(1)	Br-Mo-C(7)	113.9(2)
P(1)-Mo-C(7)	79.1(2)	P(2)-Mo-C(7)	79.2(2)
Br-Mo-C(15)	90.0(2)	P(1)-Mo-C(15)	106.0(2)
P(2)-Mo-C(15)	106.2(2)	C(7)-Mo-C(15)	156.1(2)
Br-Mo-C(16)	106.1(2)	P(1)-Mo-C(16)	79.1(2)
P(2)-Mo-C(16)	137.3(2)	C(7)-Mo-C(16)	130.6(2)
C(15)-Mo-C(16)	33.7(2)	Br-Mo-C(17)	142.3(2)
P(1)-Mo-C(17)	87.6(2)	P(2)-Mo-C(17)	125.7(2)
C(7)-Mo-C(17)	99.2(2)	C(15)-Mo-C(17)	58.4(2)
C(16)-Mo-C(17)	36.3(2)	Br-Mo-C(18)	142.2(2)
P(1)-Mo-C(18)	124.0(2)	P(2)-Mo-C(18)	89.1(2)
C(7)-Mo-C(18)	98.9(2)	C(15)-Mo-C(18)	58.6(2)
C(16)-Mo-C(18)	60.1(3)	C(17)-Mo-C(18)	36.9(3)
Br-Mo-C(19)	106.9(2)	P(1)-Mo-C(19)	136.6(2)
P(2)-Mo-C(19)	80.0(2)	C(7)-Mo-C(19)	129.4(2)
C(15)-Mo-C(19)	34.3(3)	C(16)-Mo-C(19)	57.6(3)
C(17)-Mo-C(19)	59.2(3)	C(18)-Mo-C(19)	35.3(2)
Mo-P(1)-O(1)	116.9(2)	Mo-P(1)-O(2)	121.3(2)
O(1)-P(1)-O(2)	98.2(2)	Mo-P(1)-O(3)	114.2(2)
O(1)-P(1)-O(3)	98.5(3)	O(2)-P(1)-O(3)	104.3(2)
Mo-P(2)-O(4a)	123.8(3)	Mo-P(2)-O(4b)	113.0(7)
O(4a)-P(2)-O(4b)	30.7(7)	Mo-P(2)-O(5)	112.6(2)
O(4a)-P(2)-O(5)	106.1(3)	O(4b)-P(2)-O(5)	87.3(6)
Mo-P(2)-O(6a)	113.8(3)	O(4a)-P(2)-O(6a)	100.9(4)
O(4b)-P(2)-O(6a)	127.6(7)	O(5)-P(2)-O(6a)	95.3(4)
Mo-P(2)-O(6b)	126.7(6)	O(4a)-P(2)-O(6b)	60.8(6)
O(4b)-P(2)-O(6b)	90.7(8)	O(5)-P(2)-O(6b)	115.6(6)
O(6a)-P(2)-O(6b)	41.7(6)	P(1)-O(1)-C(1)	123.2(4)
P(1)-O(2)-C(2)	122.8(4)	P(1)-O(3)-C(3)	120.6(4)
P(2)-O(4a)-O(4b)	84.7(14)	P(2)-O(4a)-O(6b)	60.9(6)
O(4b)-O(4a)-O(6b)	142.7(16)	P(2)-O(4a)-C(4)	127.2(6)
O(4b)-O(4a)-C(4)	69.0(14)	O(6b)-O(4a)-C(4)	142.9(8)
P(2)-O(4b)-O(4a)	64.6(12)	P(2)-O(4b)-C(4)	119.6(11)
O(4a)-O(4b)-C(4)	75.5(14)	P(2)-O(5)-C(5)	122.3(4)
P(2)-O(6a)-O(6b)	65.8(8)	P(2)-O(6a)-C(6)	129.3(7)
O(6b)-O(6a)-C(6)	66.5(9)	P(2)-O(6b)-O(4a)	58.4(5)
P(2)-O(6b)-O(6a)	72.5(8)	O(4a)-O(6b)-O(6a)	128.0(12)
P(2)-O(6b)-C(6)	133.3(11)	O(4a)-O(6b)-C(6)	167.9(13)
O(6a)-O(6b)-C(6)	64.0(9)	O(4a)-C(4)-O(4b)	35.6(8)
O(6a)-C(6)-O(6b)	49.5(8)	O(6a)-H(6c)-O(6b)	95.8(19)
O(6a)-H(6c)-C(6)	97.3(8)	O(6b)-H(6c)-C(6)	113.0(16)
Mo-C(7)-C(8)	177.9(5)	C(7)-C(8)-H(8)	119.3(33)
C(7)-C(8)-C(9)	127.2(5)	H(8)-C(8)-C(9)	113.5(32)
C(8)-C(9)-C(10)	120.5(5)	C(8)-C(9)-C(14)	122.3(5)
C(10)-C(9)-C(14)	117.1(5)	C(9)-C(10)-C(11)	120.9(6)
C(10)-C(11)-C(12)	120.8(6)	C(11)-C(12)-C(13)	119.3(6)
C(12)-C(13)-C(14)	120.4(6)	C(9)-C(14)-C(13)	121.4(5)
Mo-C(15)-C(16)	70.0(4)	Mo-C(15)-C(19)	71.7(4)
C(16)-C(15)-C(19)	108.9(6)	Mo-C(16)-C(15)	76.3(4)
Mo-C(16)-C(17)	68.5(4)	C(15)-C(16)-C(17)	108.5(7)
Mo-C(17)-C(16)	75.2(4)	Mo-C(17)-C(18)	72.3(4)
C(16)-C(17)-C(18)	107.4(6)	Mo-C(18)-C(17)	70.7(4)
Mo-C(18)-C(19)	76.8(4)	C(17)-C(18)-C(19)	107.0(6)
Mo-C(19)-C(15)	74.0(4)	Mo-C(19)-C(18)	67.9(4)
C(15)-C(19)-C(18)	108.2(6)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	32(1)	34(1)	34(1)	4(1)	-3(1)	1(1)
Br	38(1)	49(1)	65(1)	-9(1)	-10(1)	-5(1)
P(1)	42(1)	38(1)	44(1)	1(1)	3(1)	4(1)
P(2)	42(1)	44(1)	58(1)	-4(1)	8(1)	2(1)
O(1)	85(4)	36(2)	71(3)	-4(2)	12(3)	1(2)
O(2)	60(3)	46(2)	51(2)	2(2)	15(2)	3(2)
O(3)	35(2)	82(3)	65(3)	-5(2)	2(2)	13(2)
O(4a)	74(5)	43(3)	107(7)	16(4)	47(5)	18(3)
O(5)	40(3)	59(3)	101(4)	13(3)	21(2)	7(2)
O(6a)	131(7)	78(5)	71(5)	-16(4)	23(4)	4(4)
C(1)	77(6)	57(4)	104(7)	-3(4)	-8(5)	-12(4)
C(2)	80(5)	45(4)	59(4)	12(3)	21(4)	-1(4)
C(3)	53(5)	87(6)	101(7)	-2(5)	19(4)	4(4)
C(4)	61(5)	59(4)	81(5)	12(4)	18(4)	18(4)
C(5)	43(4)	95(6)	111(7)	14(5)	25(4)	20(4)
C(6)	258(17)	157(12)	63(6)	-41(8)	4(8)	-57(11)
C(7)	33(3)	30(3)	46(3)	4(2)	4(2)	0(2)
C(8)	39(3)	38(3)	41(3)	3(3)	-3(3)	-1(3)
C(9)	35(3)	41(3)	38(3)	-7(2)	-2(2)	5(2)
C(10)	55(4)	50(3)	43(4)	-8(3)	-10(3)	3(3)
C(11)	52(4)	69(4)	57(4)	-21(3)	-21(3)	3(3)
C(12)	51(4)	59(4)	80(5)	-26(4)	-9(3)	-8(3)
C(13)	61(4)	45(4)	73(5)	-9(3)	1(4)	-10(3)
C(14)	38(3)	49(3)	46(3)	-1(3)	-9(3)	-1(3)
C(15)	71(5)	77(5)	45(4)	22(3)	2(3)	6(4)
C(16)	74(5)	60(4)	62(4)	32(4)	8(4)	23(4)
C(17)	85(5)	43(4)	58(4)	14(3)	12(4)	-5(3)
C(18)	61(4)	67(4)	72(5)	25(4)	13(4)	-11(4)
C(19)	84(5)	70(4)	43(4)	14(3)	17(4)	11(4)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(h^2 a^{*2} U_{11} + \ldots + 2hka^*b^* U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	1189	4567	4982	86
H(1b)	2212	3737	5107	86
H(1c)	1098	3851	5657	86
H(2a)	-286	1076	5552	71
H(2b)	1316	992	5550	71
H(2c)	213	812	4753	71
H(3a)	-3105	2687	3693	82
H(3b)	-2299	3236	4437	82
H(3c)	-2597	2202	4527	82
H(4a)	3924	-569	4794	87
H(4b)	2492	-751	4206	87
H(4c)	2741	165	4683	87
H(5a)	7262	777	3345	83
H(5b)	6065	354	2692	83
H(5c)	6336	-5	3586	83
H(6a)	3235	-415	1463	136
H(6b)	2294	-782	2047	136
H(6c)	3526	-114	2374	136
H(8)	3870(55)	1537(39)	5542(33)	47(16)
H(10)	5868	1932	6564	64
H(11)	7639	2946	7081	77
H(12)	7903	4291	6399	81
H(13)	6319	4641	5203	72
H(14)	4576	3610	4650	56
H(15)	499	2381	1645	58
H(16)	106	3501	2688	61
H(17)	2487	3931	3551	68
H(18)	4361	3011	3021	74
H(19)	3101	2081	1820	84

Tables for Section 2

(I)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	2508(1)	0	1673(1)	40(1)*
Mo(2)	1314(1)	-86(1)	3437(1)	45(1)*
Cl(1)	9177(3)	1691(2)	-2603(2)	97(1)*
Cl(2)	6967(4)	605(3)	-1783(2)	145(2)*
O(1)	5210(4)	-328(3)	4487(4)	65(1)*
O(2)	-1388(8)	-921(5)	978(6)	136(3)*
O(3)	5304(4)	1826(3)	4222(3)	58(1)*
C	7616(10)	873(6)	-3052(7)	89(3)*
C(1)	4016(5)	-192(3)	3519(4)	45(1)*
C(2)	-304(9)	-565(5)	1814(6)	84(3)*
C(3)	6357(7)	1586(6)	1949(7)	94(3)*
C(4)	4759(9)	3035(4)	1717(6)	78(3)*
C(5)	3904(7)	1947(4)	-145(5)	64(2)*
C(6)	4605(6)	2003(4)	1378(5)	56(2)*
C(7)	3440(4)	1561(3)	1991(4)	37(1)*
C(8)	1701(4)	1448(3)	1191(4)	36(1)*
C(9)	585(4)	1252(3)	1827(4)	41(1)*
C(10)	953(5)	1430(4)	3193(4)	47(1)*
C(11)	2464(6)	2044(3)	3864(4)	49(2)*
C(12)	3079(8)	2032(5)	5379(5)	74(3)*
C(13)	1951(9)	3033(4)	3374(6)	71(2)*
C(14)	3884(5)	1764(3)	3435(4)	40(1)*
C(15)	2623(17)	-1471(5)	951(10)	127(6)*
C(16)	1464(14)	-974(9)	-144(10)	130(5)*
C(17)	2315(15)	-319(6)	-545(7)	101(4)*
C(18)	3932(13)	-428(5)	278(8)	92(4)*
C(19)	4105(13)	-1098(5)	1199(8)	108(4)*
C(20)	722(10)	175(6)	5372(7)	92(3)*
C(21)	-547(8)	-356(6)	4473(7)	93(3)*
C(22)	133(9)	-1213(5)	4269(7)	89(3)*
C(23)	1844(10)	-1184(5)	5063(6)	82(3)*
C(24)	2186(9)	-342(5)	5754(5)	81(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-Mo(2)	2.524(1)	Mo(1)-C(1)	1.951(4)
Mo(1)-C(7)	2.396(4)	Mo(1)-C(8)	2.222(4)
Mo(1)-C(9)	2.530(4)	Mo(1)-C(15)	2.300(8)
Mo(1)-C(16)	2.318(11)	Mo(1)-C(17)	2.405(9)
Mo(1)-C(18)	2.394(12)	Mo(1)-C(19)	2.311(10)
Mo(2)-C(1)	2.335(5)	Mo(2)-C(2)	1.918(6)
Mo(2)-C(9)	2.535(4)	Mo(2)-C(10)	2.233(5)
Mo(2)-C(20)	2.391(9)	Mo(2)-C(21)	2.347(9)
Mo(2)-C(22)	2.305(9)	Mo(2)-C(23)	2.298(7)
Mo(2)-C(24)	2.369(6)	Cl(1)-C	1.734(9)
Cl(2)-C	1.733(10)	O(1)-C(1)	1.178(5)
O(2)-C(2)	1.152(8)	O(3)-C(14)	1.208(4)
C(6)-C(3)	1.537(8)	C(6)-C(4)	1.542(8)
C(6)-C(5)	1.533(8)	C(6)-C(7)	1.559(8)
C(7)-C(8)	1.439(5)	C(7)-C(14)	1.498(6)
C(8)-H(8)	1.011(35)	C(8)-C(9)	1.428(7)
C(9)-H(9)	0.930(47)	C(9)-C(10)	1.420(6)
C(10)-H(10)	0.966(77)	C(10)-C(11)	1.527(6)
C(11)-C(12)	1.527(7)	C(11)-C(13)	1.542(7)
C(11)-C(14)	1.542(8)	C(15)-C(16)	1.428(13)
C(15)-C(19)	1.332(17)	C(16)-C(17)	1.382(17)
C(17)-C(18)	1.358(14)	C(18)-C(19)	1.367(12)
C(20)-C(21)	1.394(10)	C(20)-C(24)	1.402(11)
C(21)-C(22)	1.437(12)	C(22)-C(23)	1.408(10)
C(23)-C(24)	1.411(10)		

(I)

Table 3. Bond angles (°)

Mo(2)-Mo(1)-C(1)	61.3(2)	Mo(2)-Mo(1)-C(7)	98.9(1)
C(1)-Mo(1)-C(7)	86.1(1)	Mo(2)-Mo(1)-C(8)	92.3(1)
C(1)-Mo(1)-C(8)	113.9(1)	C(7)-Mo(1)-C(8)	36.1(1)
Mo(2)-Mo(1)-C(9)	60.2(1)	C(1)-Mo(1)-C(9)	103.6(2)
C(7)-Mo(1)-C(9)	60.2(1)	C(8)-Mo(1)-C(9)	34.2(2)
Mo(2)-Mo(1)-C(15)	107.5(3)	C(1)-Mo(1)-C(15)	96.8(3)
C(7)-Mo(1)-C(15)	151.3(4)	C(8)-Mo(1)-C(15)	148.9(3)
C(9)-Mo(1)-C(15)	144.5(4)	Mo(2)-Mo(1)-C(16)	118.7(3)
C(1)-Mo(1)-C(16)	132.7(3)	C(7)-Mo(1)-C(16)	134.7(3)
C(8)-Mo(1)-C(16)	113.3(3)	C(9)-Mo(1)-C(16)	116.6(3)
C(15)-Mo(1)-C(16)	36.0(4)	Mo(2)-Mo(1)-C(17)	150.4(3)
C(1)-Mo(1)-C(17)	139.9(3)	C(7)-Mo(1)-C(17)	102.5(3)
C(8)-Mo(1)-C(17)	93.1(2)	C(9)-Mo(1)-C(17)	114.7(3)
C(15)-Mo(1)-C(17)	58.0(3)	C(16)-Mo(1)-C(17)	34.0(4)
Mo(2)-Mo(1)-C(18)	160.6(2)	C(1)-Mo(1)-C(18)	108.0(2)
C(7)-Mo(1)-C(18)	96.2(2)	C(8)-Mo(1)-C(18)	107.0(2)
C(9)-Mo(1)-C(18)	138.9(2)	C(15)-Mo(1)-C(18)	55.7(4)
C(16)-Mo(1)-C(18)	55.0(4)	C(17)-Mo(1)-C(18)	32.9(3)
Mo(2)-Mo(1)-C(19)	127.0(2)	C(1)-Mo(1)-C(19)	84.6(2)
C(7)-Mo(1)-C(19)	119.3(3)	C(8)-Mo(1)-C(19)	140.2(3)
C(9)-Mo(1)-C(19)	171.5(2)	C(15)-Mo(1)-C(19)	33.6(4)
C(16)-Mo(1)-C(19)	57.0(3)	C(17)-Mo(1)-C(19)	56.8(3)
C(18)-Mo(1)-C(19)	33.7(3)	Mo(1)-Mo(2)-C(1)	47.2(1)
Mo(1)-Mo(2)-C(2)	71.9(3)	C(1)-Mo(2)-C(2)	112.6(3)
Mo(1)-Mo(2)-C(9)	60.0(1)	C(1)-Mo(2)-C(9)	93.2(1)
C(2)-Mo(2)-C(9)	75.1(2)	Mo(1)-Mo(2)-C(10)	86.6(1)
C(1)-Mo(2)-C(10)	99.4(2)	C(2)-Mo(2)-C(10)	103.3(2)
C(9)-Mo(2)-C(10)	33.9(2)	Mo(1)-Mo(2)-C(20)	163.9(2)
C(1)-Mo(2)-C(20)	122.7(2)	C(2)-Mo(2)-C(20)	122.5(3)
C(9)-Mo(2)-C(20)	114.0(2)	C(10)-Mo(2)-C(20)	83.1(2)
Mo(1)-Mo(2)-C(21)	160.9(2)	C(1)-Mo(2)-C(21)	148.4(2)
C(2)-Mo(2)-C(21)	89.0(3)	C(9)-Mo(2)-C(21)	115.3(2)
C(10)-Mo(2)-C(21)	97.5(3)	C(20)-Mo(2)-C(21)	34.2(3)
Mo(1)-Mo(2)-C(22)	135.8(2)	C(1)-Mo(2)-C(22)	122.7(2)
C(2)-Mo(2)-C(22)	79.7(3)	C(9)-Mo(2)-C(22)	142.2(2)
C(10)-Mo(2)-C(22)	133.4(3)	C(20)-Mo(2)-C(22)	58.8(3)
C(21)-Mo(2)-C(22)	36.0(3)	Mo(1)-Mo(2)-C(23)	127.2(2)
C(1)-Mo(2)-C(23)	91.6(2)	C(2)-Mo(2)-C(23)	108.3(3)
C(9)-Mo(2)-C(23)	172.5(2)	C(10)-Mo(2)-C(23)	139.3(2)
C(20)-Mo(2)-C(23)	58.5(3)	C(21)-Mo(2)-C(23)	58.8(3)
C(22)-Mo(2)-C(23)	35.6(3)	Mo(1)-Mo(2)-C(24)	139.9(2)
C(1)-Mo(2)-C(24)	92.7(2)	C(2)-Mo(2)-C(24)	138.1(3)
C(9)-Mo(2)-C(24)	138.6(2)	C(10)-Mo(2)-C(24)	104.8(2)
C(20)-Mo(2)-C(24)	34.3(3)	C(21)-Mo(2)-C(24)	57.0(2)
C(22)-Mo(2)-C(24)	58.4(3)	C(23)-Mo(2)-C(24)	35.2(3)
Cl(1)-C-Cl(2)	113.3(4)	Mo(1)-C(1)-Mo(2)	71.5(1)
Mo(1)-C(1)-O(1)	163.2(5)	Mo(2)-C(1)-O(1)	125.2(4)
Mo(2)-C(2)-O(2)	168.4(7)	C(3)-C(6)-C(7)	112.1(5)
C(4)-C(6)-C(7)	108.1(5)	C(5)-C(6)-C(7)	113.0(4)
Mo(1)-C(7)-C(6)	124.9(3)	Mo(1)-C(7)-C(8)	65.3(2)
C(6)-C(7)-C(8)	120.0(3)	Mo(1)-C(7)-C(14)	105.9(3)
C(6)-C(7)-C(14)	115.1(3)	C(8)-C(7)-C(14)	116.2(4)
Mo(1)-C(8)-C(7)	78.6(2)	Mo(1)-C(8)-H(8)	110.3(22)
C(7)-C(8)-H(8)	119.8(22)	Mo(1)-C(8)-C(9)	84.8(3)
C(7)-C(8)-C(9)	119.3(3)	H(8)-C(8)-C(9)	120.8(22)
Mo(1)-C(9)-Mo(2)	59.8(1)	Mo(1)-C(9)-C(8)	61.0(2)
Mo(2)-C(9)-C(8)	117.1(3)	Mo(1)-C(9)-H(9)	107.8(35)
Mo(2)-C(9)-H(9)	101.8(33)	C(8)-C(9)-H(9)	114.6(38)
Mo(1)-C(9)-C(10)	108.4(3)	Mo(2)-C(9)-C(10)	61.3(3)
C(8)-C(9)-C(10)	123.6(3)	H(9)-C(9)-C(10)	120.8(38)
Mo(2)-C(10)-C(9)	84.8(3)	Mo(2)-C(10)-H(10)	115.1(46)
C(9)-C(10)-H(10)	115.2(35)	Mo(2)-C(10)-C(11)	117.8(3)
C(9)-C(10)-C(11)	114.3(4)	H(10)-C(10)-C(11)	108.3(39)
C(10)-C(11)-C(12)	112.8(5)	C(10)-C(11)-C(13)	107.5(4)
C(10)-C(11)-C(14)	110.4(4)	C(12)-C(11)-C(14)	109.8(4)
C(13)-C(11)-C(14)	107.6(5)	O(3)-C(14)-C(7)	122.4(4)
O(3)-C(14)-C(11)	119.4(4)	C(7)-C(14)-C(11)	117.5(3)
Mo(1)-C(15)-C(16)	72.7(6)	Mo(1)-C(15)-C(19)	73.7(5)
C(16)-C(15)-C(19)	106.3(9)	Mo(1)-C(16)-C(15)	71.3(5)
Mo(1)-C(16)-C(17)	76.5(6)	C(15)-C(16)-C(17)	108.7(10)
Mo(1)-C(17)-C(16)	69.6(6)	Mo(1)-C(17)-C(18)	73.1(6)
C(16)-C(17)-C(18)	105.1(8)	Mo(1)-C(18)-C(17)	74.0(7)
Mo(1)-C(18)-C(19)	69.8(7)	C(17)-C(18)-C(19)	111.0(10)
Mo(1)-C(19)-C(15)	72.7(6)	Mo(1)-C(19)-C(18)	76.5(6)
C(15)-C(19)-C(18)	108.8(8)	Mo(2)-C(20)-C(21)	71.2(5)
Mo(2)-C(20)-C(24)	72.0(5)	C(21)-C(20)-C(24)	107.3(7)
Mo(2)-C(21)-C(20)	74.6(5)	Mo(2)-C(21)-C(22)	70.4(5)
C(20)-C(21)-C(22)	109.0(6)	Mo(2)-C(22)-C(21)	73.6(5)
Mo(2)-C(22)-C(23)	71.9(5)	C(21)-C(22)-C(23)	106.5(6)
Mo(2)-C(23)-C(22)	72.5(4)	Mo(2)-C(23)-C(24)	75.2(4)
C(22)-C(23)-C(24)	107.9(7)	Mo(2)-C(24)-C(20)	73.7(4)
Mo(2)-C(24)-C(23)	69.7(4)	C(20)-C(24)-C(23)	109.2(6)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	51(1)	36(1)	38(1)	-3(1)	23(1)	-1(1)
Mo(2)	43(1)	55(1)	44(1)	7(1)	23(1)	-4(1)
Cl(1)	103(1)	90(1)	90(1)	-17(1)	27(1)	-7(1)
Cl(2)	164(2)	186(3)	81(1)	13(2)	44(1)	-49(2)
O(1)	55(2)	66(2)	66(2)	17(2)	13(2)	18(2)
O(2)	117(4)	158(6)	93(3)	8(4)	-4(3)	-97(4)
O(3)	43(2)	67(2)	51(2)	7(2)	5(1)	-5(2)
C	99(5)	89(5)	64(4)	-6(3)	15(4)	5(4)
C(1)	51(2)	31(2)	55(2)	7(2)	25(2)	9(2)
C(2)	89(4)	90(5)	60(3)	4(3)	16(3)	-48(4)
C(3)	44(3)	136(7)	113(5)	37(5)	43(3)	9(4)
C(4)	88(4)	61(3)	74(4)	14(3)	21(3)	-29(3)
C(5)	71(3)	70(3)	68(3)	18(3)	45(3)	-3(3)
C(6)	41(2)	65(3)	69(3)	23(2)	29(2)	-1(2)
C(7)	33(2)	33(2)	46(2)	6(1)	18(1)	1(1)
C(8)	31(2)	40(2)	36(2)	5(1)	12(1)	5(1)
C(9)	29(2)	51(2)	45(2)	7(2)	15(2)	1(2)
C(10)	38(2)	60(3)	50(2)	2(2)	23(2)	12(2)
C(11)	55(2)	48(2)	42(2)	-6(2)	17(2)	10(2)
C(12)	91(4)	84(4)	47(3)	-15(3)	27(3)	12(3)
C(13)	92(4)	43(2)	73(3)	-8(2)	27(3)	18(3)
C(14)	38(2)	34(2)	40(2)	3(1)	7(2)	-0(1)
C(15)	260(12)	45(3)	118(6)	-32(4)	118(8)	-25(5)
C(16)	129(7)	142(9)	112(7)	-93(7)	39(6)	-37(7)
C(17)	170(8)	92(5)	52(3)	-20(3)	55(4)	8(6)
C(18)	147(7)	74(4)	97(5)	-9(4)	93(5)	21(4)
C(19)	184(8)	66(4)	97(5)	0(4)	80(6)	54(5)
C(20)	130(5)	99(6)	87(4)	26(4)	86(4)	21(4)
C(21)	78(4)	132(7)	96(5)	31(5)	63(4)	-2(4)
C(22)	100(5)	88(5)	101(5)	34(4)	61(4)	-12(4)
C(23)	107(5)	81(4)	71(4)	31(3)	49(4)	10(4)
C(24)	94(4)	112(5)	49(3)	20(3)	38(3)	6(4)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2 a^{*2} U_{11} + \ldots + 2hka^*b^* U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(3a)	6817	1644	2901	109
H(3b)	7040	1912	1588	109
H(3c)	6314	949	1711	109
H(4a)	5093	3214	2632	96
H(4b)	3692	3296	1204	96
H(4c)	5558	3253	1382	96
H(5a)	3779	1316	-422	74
H(5b)	4610	2255	-503	74
H(5c)	2836	2238	-465	74
H(8)	1273(42)	1551(26)	197(34)	20(8)
H(9)	-486(62)	1102(37)	1249(51)	50(13)
H(10)	43(81)	1672(51)	3386(61)	95(19)
H(12a)	2112	2080	5588	89
H(12b)	3809	2538	5770	89
H(12c)	3642	1466	5727	89
H(13a)	2872	3445	3755	85
H(13b)	1019	3260	3540	85
H(13c)	1660	2990	2432	85
H(15)	2382	-1974	1416	150
H(16)	288	-1078	-538	142
H(17)	1860	119	-1252	125
H(18)	4834	-80	220	140
H(19)	5125	-1273	1907	140
H(20)	612	781	5673	105
H(21)	-1691	-177	4056	113
H(22)	-462	-1707	3703	108
H(23)	2637	-1656	5123	104
H(24)	3252	-152	6386	96

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	3049(1)	1014(1)	1202(1)	28(1)*
Mo(2)	-280(1)	-3258(1)	3376(1)	30(1)*
O(5)	1228(3)	-172(3)	1841(2)	33(1)*
O(6)	2850(4)	-2274(4)	422(2)	61(1)*
O(7)	6667(4)	724(4)	1494(2)	62(1)*
O(8)	-2891(4)	-4669(4)	4446(2)	54(1)*
O(9)	1050(5)	-1917(4)	5225(2)	69(1)*
C(1)	5280(6)	2631(5)	2944(3)	48(2)*
C(2)	3793(5)	1537(4)	2561(3)	32(1)*
C(3)	2758(5)	910(4)	3099(2)	32(1)*
C(4)	3039(6)	1159(6)	4078(3)	48(2)*
C(5)	1338(5)	24(4)	2660(2)	30(1)*
C(6)	-40(5)	-649(4)	3071(2)	31(1)*
C(7)	-1403(4)	-1491(4)	2570(2)	29(1)*
C(8)	-2757(5)	-2189(4)	2909(3)	32(1)*
C(9)	-4051(5)	-3201(5)	2309(3)	41(1)*
C(10)	-3369(5)	-1416(5)	3606(3)	44(2)*
C(11)	1150(6)	2648(6)	642(3)	50(2)*
C(12)	2556(6)	3558(5)	1048(3)	51(2)*
C(13)	3810(6)	3355(5)	604(3)	46(2)*
C(14)	3181(6)	2289(5)	-71(3)	46(2)*
C(15)	1510(5)	1842(5)	-51(3)	44(2)*
C(16)	2896(5)	-1085(5)	712(3)	40(2)*
C(17)	5325(5)	790(5)	1405(3)	40(1)*
C(18)	-1949(5)	-4153(5)	4038(3)	38(1)*
C(19)	561(5)	-2387(5)	4526(3)	45(2)*
C(20)	-338(7)	-5376(7)	2504(5)	88(3)*
C(21)	708(9)	-5521(7)	3307(4)	85(3)*
C(22)	1988(7)	-4421(8)	3333(4)	73(3)*
C(23)	1787(7)	-3592(7)	2609(4)	69(2)*
C(24)	393(8)	-4124(7)	2089(4)	68(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-O(5)	2.132(3)	Mo(1)-C(2)	2.158(4)
Mo(1)-C(11)	2.404(5)	Mo(1)-C(12)	2.371(5)
Mo(1)-C(13)	2.318(4)	Mo(1)-C(14)	2.293(5)
Mo(1)-C(15)	2.356(4)	Mo(1)-C(16)	2.008(5)
Mo(1)-C(17)	1.969(5)	Mo(2)-C(6)	2.349(4)
Mo(2)-C(7)	2.239(4)	Mo(2)-C(8)	2.463(4)
Mo(2)-C(18)	1.971(4)	Mo(2)-C(19)	1.954(4)
Mo(2)-C(20)	2.337(7)	Mo(2)-C(21)	2.318(7)
Mo(2)-C(22)	2.357(7)	Mo(2)-C(23)	2.363(7)
Mo(2)-C(24)	2.364(6)	O(5)-C(5)	1.286(4)
O(6)-C(16)	1.152(6)	O(7)-C(17)	1.149(6)
O(8)-C(18)	1.151(6)	O(9)-C(19)	1.165(5)
C(2)-C(1)	1.521(5)	C(2)-C(3)	1.378(6)
C(3)-C(4)	1.530(6)	C(3)-C(5)	1.420(5)
C(5)-C(6)	1.481(6)	C(6)-H(6)	0.742(35)
C(6)-C(7)	1.409(5)	C(7)-H(7)	0.896(37)
C(7)-C(8)	1.411(6)	C(8)-C(9)	1.515(5)
C(8)-C(10)	1.510(7)	C(11)-C(12)	1.405(6)
C(11)-C(15)	1.416(7)	C(12)-C(13)	1.413(8)
C(13)-C(14)	1.411(6)	C(14)-C(15)	1.433(7)
C(20)-C(21)	1.437(9)	C(20)-C(24)	1.398(9)
C(21)-C(22)	1.349(9)	C(22)-C(23)	1.347(9)
C(23)-C(24)	1.353(8)		

(II)

Table 3. Bond angles (°)

O(5)-Mo(1)-C(2)	73.6(1)	O(5)-Mo(1)-C(11)	86.6(1)
C(2)-Mo(1)-C(11)	107.4(2)	O(5)-Mo(1)-C(12)	106.5(2)
C(2)-Mo(1)-C(12)	86.4(2)	C(11)-Mo(1)-C(12)	34.2(2)
O(5)-Mo(1)-C(13)	141.2(2)	C(2)-Mo(1)-C(13)	100.9(1)
C(11)-Mo(1)-C(13)	57.8(2)	C(12)-Mo(1)-C(13)	35.1(2)
O(5)-Mo(1)-C(14)	137.0(1)	C(2)-Mo(1)-C(14)	136.4(1)
C(11)-Mo(1)-C(14)	58.3(2)	C(12)-Mo(1)-C(14)	58.6(2)
C(13)-Mo(1)-C(14)	35.6(2)	O(5)-Mo(1)-C(15)	101.2(1)
C(2)-Mo(1)-C(15)	141.6(2)	C(11)-Mo(1)-C(15)	34.6(2)
C(12)-Mo(1)-C(15)	58.0(2)	C(13)-Mo(1)-C(15)	59.0(2)
C(14)-Mo(1)-C(15)	35.9(2)	O(5)-Mo(1)-C(16)	80.2(2)
C(2)-Mo(1)-C(16)	122.6(2)	C(11)-Mo(1)-C(16)	121.2(2)
C(12)-Mo(1)-C(16)	150.6(2)	C(13)-Mo(1)-C(16)	129.5(2)
C(14)-Mo(1)-C(16)	96.6(2)	C(15)-Mo(1)-C(16)	92.8(2)
O(5)-Mo(1)-C(17)	126.7(1)	C(2)-Mo(1)-C(17)	76.7(2)
C(11)-Mo(1)-C(17)	145.0(2)	C(12)-Mo(1)-C(17)	114.7(2)
C(13)-Mo(1)-C(17)	87.1(2)	C(14)-Mo(1)-C(17)	94.2(2)
C(15)-Mo(1)-C(17)	128.7(2)	C(16)-Mo(1)-C(17)	79.9(2)
C(6)-Mo(2)-C(7)	35.7(1)	C(6)-Mo(2)-C(8)	62.3(1)
C(7)-Mo(2)-C(8)	34.5(1)	C(6)-Mo(2)-C(18)	118.4(2)
C(7)-Mo(2)-C(18)	103.7(2)	C(8)-Mo(2)-C(18)	69.5(2)
C(6)-Mo(2)-C(19)	79.3(2)	C(7)-Mo(2)-C(19)	108.0(2)
C(8)-Mo(2)-C(19)	104.7(2)	C(18)-Mo(2)-C(19)	78.2(2)
C(6)-Mo(2)-C(20)	131.7(2)	C(7)-Mo(2)-C(20)	108.8(2)
C(8)-Mo(2)-C(20)	108.3(2)	C(18)-Mo(2)-C(20)	97.7(2)
C(19)-Mo(2)-C(20)	142.9(2)	C(6)-Mo(2)-C(21)	148.0(2)
C(7)-Mo(2)-C(21)	143.5(2)	C(8)-Mo(2)-C(21)	139.8(2)
C(18)-Mo(2)-C(21)	93.5(2)	C(19)-Mo(2)-C(21)	107.0(2)
C(20)-Mo(2)-C(21)	36.0(2)	C(6)-Mo(2)-C(22)	116.7(2)
C(7)-Mo(2)-C(22)	133.6(2)	C(8)-Mo(2)-C(22)	161.2(2)
C(18)-Mo(2)-C(22)	121.1(2)	C(19)-Mo(2)-C(22)	93.1(2)
C(20)-Mo(2)-C(22)	57.1(2)	C(21)-Mo(2)-C(22)	33.5(2)
C(6)-Mo(2)-C(23)	92.5(2)	C(7)-Mo(2)-C(23)	100.7(2)
C(8)-Mo(2)-C(23)	130.4(2)	C(18)-Mo(2)-C(23)	149.0(2)
C(19)-Mo(2)-C(23)	111.9(2)	C(20)-Mo(2)-C(23)	56.1(2)
C(21)-Mo(2)-C(23)	55.8(2)	C(22)-Mo(2)-C(23)	33.2(2)
C(6)-Mo(2)-C(24)	98.7(2)	C(7)-Mo(2)-C(24)	86.9(2)
C(8)-Mo(2)-C(24)	104.9(2)	C(18)-Mo(2)-C(24)	129.9(2)
C(19)-Mo(2)-C(24)	145.1(2)	C(20)-Mo(2)-C(24)	34.6(2)
C(21)-Mo(2)-C(24)	57.9(2)	C(22)-Mo(2)-C(24)	56.3(2)
C(23)-Mo(2)-C(24)	33.3(2)	Mo(1)-O(5)-C(5)	118.8(2)
Mo(1)-C(2)-C(1)	124.9(3)	Mo(1)-C(2)-C(3)	116.1(3)
C(1)-C(2)-C(3)	118.7(4)	C(2)-C(3)-C(4)	124.6(3)
C(2)-C(3)-C(5)	113.9(3)	C(4)-C(3)-C(5)	121.5(4)
O(5)-C(5)-C(3)	117.2(4)	O(5)-C(5)-C(6)	117.8(3)
C(3)-C(5)-C(6)	125.0(3)	Mo(2)-C(6)-C(5)	117.1(3)
Mo(2)-C(6)-H(6)	105.5(26)	C(5)-C(6)-H(6)	112.4(25)
Mo(2)-C(6)-C(7)	67.9(2)	C(5)-C(6)-C(7)	120.2(3)
H(6)-C(6)-C(7)	123.6(26)	Mo(2)-C(7)-C(6)	76.4(2)
Mo(2)-C(7)-H(7)	109.4(24)	C(6)-C(7)-H(7)	117.6(22)
Mo(2)-C(7)-C(8)	81.4(2)	C(6)-C(7)-C(8)	124.0(3)
H(7)-C(7)-C(8)	118.2(22)	Mo(2)-C(8)-C(7)	64.0(2)
Mo(2)-C(8)-C(9)	115.2(3)	C(7)-C(8)-C(9)	117.7(4)
Mo(2)-C(8)-C(10)	115.7(3)	C(7)-C(8)-C(10)	121.0(3)
Mo(1)-C(11)-C(12)	71.6(3)	Mo(1)-C(11)-C(15)	70.9(3)
C(12)-C(11)-C(15)	108.7(4)	Mo(1)-C(12)-C(11)	74.2(3)
Mo(1)-C(12)-C(13)	70.4(3)	C(11)-C(12)-C(13)	108.3(4)
Mo(1)-C(13)-C(12)	74.5(3)	Mo(1)-C(13)-C(14)	71.2(3)
C(12)-C(13)-C(14)	108.0(4)	Mo(1)-C(14)-C(13)	73.1(3)
Mo(1)-C(14)-C(15)	74.5(3)	C(13)-C(14)-C(15)	108.1(4)
Mo(1)-C(15)-C(11)	74.6(3)	Mo(1)-C(15)-C(14)	69.7(2)
C(11)-C(15)-C(14)	106.9(4)	Mo(1)-C(16)-O(6)	178.0(4)
Mo(1)-C(17)-O(7)	176.3(4)	Mo(2)-C(18)-O(8)	178.0(3)
Mo(2)-C(19)-O(9)	177.6(4)	Mo(2)-C(20)-C(21)	71.3(4)
Mo(2)-C(20)-C(24)	73.8(4)	C(21)-C(20)-C(24)	106.1(5)
Mo(2)-C(21)-C(20)	72.7(4)	Mo(2)-C(21)-C(22)	74.8(4)
C(20)-C(21)-C(22)	107.3(6)	Mo(2)-C(22)-C(21)	71.6(4)
Mo(2)-C(22)-C(23)	73.7(4)	C(21)-C(22)-C(23)	108.6(5)
Mo(2)-C(23)-C(22)	73.2(4)	Mo(2)-C(23)-C(24)	73.4(4)
C(22)-C(23)-C(24)	111.2(5)	Mo(2)-C(24)-C(20)	71.6(4)
Mo(2)-C(24)-C(23)	73.3(4)	C(20)-C(24)-C(23)	106.8(5)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	26(1)	33(1)	26(1)	2(1)	8(1)	4(1)
Mo(2)	27(1)	36(1)	29(1)	5(1)	8(1)	8(1)
O(5)	30(1)	42(2)	25(1)	-1(1)	8(1)	-2(1)
O(6)	68(2)	47(2)	71(2)	-16(2)	14(2)	13(2)
O(7)	35(2)	83(3)	73(2)	11(2)	11(2)	21(2)
O(8)	49(2)	62(2)	53(2)	13(2)	25(2)	-5(2)
O(9)	82(3)	75(2)	38(2)	-4(2)	-6(2)	-8(2)
C(1)	43(3)	49(3)	44(3)	-0(2)	2(2)	-7(2)
C(2)	30(2)	31(2)	32(2)	2(2)	5(2)	3(2)
C(3)	34(2)	32(2)	29(2)	2(2)	5(2)	0(2)
C(4)	51(3)	55(3)	31(2)	-3(2)	4(2)	-4(2)
C(5)	34(2)	31(2)	26(2)	2(2)	8(2)	6(2)
C(6)	36(2)	38(2)	21(2)	-1(2)	11(2)	5(2)
C(7)	29(2)	34(2)	26(2)	7(2)	10(2)	9(2)
C(8)	26(2)	38(2)	35(2)	8(2)	10(2)	10(2)
C(9)	28(2)	53(3)	40(2)	6(2)	7(2)	2(2)
C(10)	39(3)	49(3)	52(3)	4(2)	23(2)	13(2)
C(11)	41(3)	67(3)	49(3)	11(2)	11(2)	26(2)
C(12)	66(3)	44(3)	46(3)	-2(2)	6(2)	23(2)
C(13)	42(3)	41(2)	51(3)	12(2)	7(2)	1(2)
C(14)	52(3)	52(3)	38(2)	16(2)	18(2)	14(2)
C(15)	45(3)	53(3)	32(2)	7(2)	2(2)	9(2)
C(16)	36(2)	48(3)	39(2)	3(2)	14(2)	7(2)
C(17)	42(2)	44(2)	33(2)	2(2)	4(2)	7(2)
C(18)	38(2)	39(2)	35(2)	1(2)	1(2)	6(2)
C(19)	46(3)	47(3)	38(2)	10(2)	5(2)	-3(2)
C(20)	51(3)	69(4)	152(6)	-62(4)	40(4)	3(3)
C(21)	118(6)	67(4)	105(5)	46(4)	77(5)	61(4)
C(22)	51(3)	101(5)	78(4)	3(4)	11(3)	48(4)
C(23)	63(4)	62(3)	104(5)	16(3)	55(4)	30(3)
C(24)	82(4)	94(4)	48(3)	3(3)	26(3)	57(4)

The anisotropic temperature factor exponent takes the form:

$2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(1a)	5655	3217	2480	55
H(1b)	6108	2101	3230	55
H(1c)	5002	3297	3350	55
H(4a)	3938	1902	4314	57
H(4b)	3168	186	4327	57
H(4c)	2076	1453	4207	57
H(6)	-53(41)	-268(37)	3485(22)	20(9)
H(7)	-1370(43)	-1656(40)	2012(23)	27(10)
H(9a)	-4644	-3911	2648	52
H(9b)	-3605	-3745	1911	52
H(9c)	-4752	-2569	1993	52
H(10a)	-2508	-755	3948	51
H(10b)	-3843	-2169	3970	51
H(10c)	-4161	-832	3336	51
H(11)	115	2583	808	62
H(12)	2649	4207	1542	56
H(13)	4898	3855	737	57
H(14)	3770	1927	-472	55
H(15)	776	1130	-436	50
H(20)	-1337	-6010	2295	90
H(21)	529	-6265	3744	83
H(22)	2892	-4256	3790	87
H(23)	2534	-2734	2479	78
H(24)	-16	-3721	1541	78

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	263(1)	1695(1)	1878(1)	36(1)*
Mo(2)	5061(1)	3443(1)	2548(1)	29(1)*
O(1)	633(4)	1363(2)	-101(2)	97(2)*
O(2)	-735(3)	3481(2)	695(2)	87(1)*
O(3)	5170(2)	1658(1)	1442(2)	54(1)*
O(4)	6499(3)	4131(2)	1180(2)	78(1)*
C(1)	524(4)	1470(2)	645(3)	55(1)*
C(2)	-377(3)	2833(2)	1146(2)	54(1)*
C(3)	2504(3)	1387(2)	2488(2)	41(1)*
C(4)	2377(3)	2348(2)	2469(2)	33(1)*
C(5)	1641(3)	2704(2)	3011(2)	43(1)*
C(6)	2860(3)	2903(2)	1810(2)	31(1)*
C(7)	2929(3)	3873(2)	1841(2)	33(1)*
C(8)	3504(3)	4358(2)	1259(2)	35(1)*
C(9)	3640(3)	5384(2)	1389(2)	50(1)*
C(10)	3295(3)	4048(2)	227(2)	48(1)*
C(11)	-1807(4)	1052(3)	1561(3)	68(2)*
C(12)	-1501(4)	1557(3)	2429(3)	69(2)*
C(13)	-431(4)	1138(3)	3146(3)	70(2)*
C(14)	-45(4)	390(3)	2755(3)	75(2)*
C(15)	-889(5)	329(3)	1755(3)	79(2)*
C(16)	4947(4)	3709(4)	4108(2)	82(2)*
C(17)	5703(5)	4415(2)	3932(2)	84(2)*
C(18)	6828(5)	4023(4)	3875(3)	92(2)*
C(19)	6768(5)	3111(4)	4011(3)	88(2)*
C(20)	5640(5)	2916(3)	4154(2)	74(2)*
C(21)	5137(3)	2325(2)	1866(2)	36(1)*
C(22)	5939(3)	3883(2)	1677(2)	47(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-C(1)	1.952(4)	Mo(1)-C(2)	1.969(3)
Mo(1)-C(3)	2.290(3)	Mo(1)-C(4)	2.325(3)
Mo(1)-C(5)	2.318(3)	Mo(1)-C(11)	2.302(4)
Mo(1)-C(12)	2.318(4)	Mo(1)-C(13)	2.381(5)
Mo(1)-C(14)	2.392(5)	Mo(1)-C(15)	2.325(4)
Mo(2)-C(6)	2.356(2)	Mo(2)-C(7)	2.238(3)
Mo(2)-C(8)	2.428(2)	Mo(2)-C(16)	2.365(4)
Mo(2)-C(17)	2.370(3)	Mo(2)-C(18)	2.336(4)
Mo(2)-C(19)	2.318(4)	Mo(2)-C(20)	2.340(3)
Mo(2)-C(21)	1.936(3)	Mo(2)-C(22)	1.948(4)
O(1)-C(1)	1.152(5)	O(2)-C(2)	1.141(4)
O(3)-C(21)	1.165(4)	O(4)-C(22)	1.156(5)
C(3)-H(3a)	0.959(32)	C(3)-H(3b)	0.947(35)
C(3)-C(4)	1.414(4)	C(4)-C(5)	1.405(5)
C(4)-C(6)	1.489(4)	C(5)-H(5a)	0.954(29)
C(5)-H(5b)	0.959(32)	C(6)-H(6)	0.964(26)
C(6)-C(7)	1.423(4)	C(7)-H(7)	0.903(26)
C(7)-C(8)	1.410(4)	C(8)-C(9)	1.517(4)
C(8)-C(10)	1.517(4)	C(11)-C(12)	1.406(6)
C(11)-C(15)	1.404(6)	C(12)-C(13)	1.392(5)
C(13)-C(14)	1.367(7)	C(14)-C(15)	1.424(6)
C(16)-C(17)	1.394(7)	C(16)-C(20)	1.369(7)
C(17)-C(18)	1.367(8)	C(18)-C(19)	1.355(8)
C(19)-C(20)	1.331(7)		

(III)

Table 3. Bond angles (°)

C(1)-Mo(1)-C(2)	77.1(2)	C(1)-Mo(1)-C(3)	81.4(1)
C(2)-Mo(1)-C(3)	119.5(1)	C(1)-Mo(1)-C(4)	88.3(1)
C(2)-Mo(1)-C(4)	87.6(1)	C(3)-Mo(1)-C(4)	35.7(1)
C(1)-Mo(1)-C(5)	120.3(1)	C(2)-Mo(1)-C(5)	81.9(1)
C(3)-Mo(1)-C(5)	62.3(1)	C(4)-Mo(1)-C(5)	35.2(1)
C(1)-Mo(1)-C(11)	101.0(1)	C(2)-Mo(1)-C(11)	96.5(1)
C(3)-Mo(1)-C(11)	143.2(1)	C(4)-Mo(1)-C(11)	170.4(1)
C(5)-Mo(1)-C(11)	136.7(1)	C(1)-Mo(1)-C(12)	135.5(1)
C(2)-Mo(1)-C(12)	95.4(2)	C(3)-Mo(1)-C(12)	136.1(1)
C(4)-Mo(1)-C(12)	135.7(1)	C(5)-Mo(1)-C(12)	101.4(1)
C(11)-Mo(1)-C(12)	35.4(1)	C(1)-Mo(1)-C(13)	148.5(2)
C(2)-Mo(1)-C(13)	124.8(2)	C(3)-Mo(1)-C(13)	101.9(1)
C(4)-Mo(1)-C(13)	112.7(1)	C(5)-Mo(1)-C(13)	87.6(1)
C(11)-Mo(1)-C(13)	57.9(1)	C(12)-Mo(1)-C(13)	34.4(1)
C(1)-Mo(1)-C(14)	117.1(2)	C(2)-Mo(1)-C(14)	151.8(2)
C(3)-Mo(1)-C(14)	87.7(1)	C(4)-Mo(1)-C(14)	115.7(1)
C(5)-Mo(1)-C(14)	107.5(1)	C(11)-Mo(1)-C(14)	58.1(1)
C(12)-Mo(1)-C(14)	57.0(2)	C(13)-Mo(1)-C(14)	33.3(2)
C(1)-Mo(1)-C(15)	91.7(2)	C(2)-Mo(1)-C(15)	127.9(1)
C(3)-Mo(1)-C(15)	108.4(1)	C(4)-Mo(1)-C(15)	143.5(1)
C(5)-Mo(1)-C(15)	142.2(1)	C(11)-Mo(1)-C(15)	35.3(2)
C(12)-Mo(1)-C(15)	58.3(2)	C(13)-Mo(1)-C(15)	57.3(2)
C(14)-Mo(1)-C(15)	35.1(1)	C(6)-Mo(2)-C(7)	36.0(1)
C(6)-Mo(2)-C(8)	62.0(1)	C(7)-Mo(2)-C(8)	34.9(1)
C(6)-Mo(2)-C(16)	96.2(1)	C(7)-Mo(2)-C(16)	90.2(1)
C(8)-Mo(2)-C(16)	113.7(1)	C(6)-Mo(2)-C(17)	122.1(2)
C(7)-Mo(2)-C(17)	99.4(1)	C(8)-Mo(2)-C(17)	104.1(1)
C(16)-Mo(2)-C(17)	34.2(2)	C(6)-Mo(2)-C(18)	152.4(2)
C(7)-Mo(2)-C(18)	132.4(2)	C(8)-Mo(2)-C(18)	125.1(2)
C(16)-Mo(2)-C(18)	56.1(2)	C(17)-Mo(2)-C(18)	33.8(2)
C(6)-Mo(2)-C(19)	133.2(1)	C(7)-Mo(2)-C(19)	145.7(2)
C(8)-Mo(2)-C(19)	158.6(1)	C(16)-Mo(2)-C(19)	55.8(2)
C(17)-Mo(2)-C(19)	56.2(2)	C(18)-Mo(2)-C(19)	33.8(2)
C(6)-Mo(2)-C(20)	102.2(1)	C(7)-Mo(2)-C(20)	114.7(2)
C(8)-Mo(2)-C(20)	145.7(1)	C(16)-Mo(2)-C(20)	33.8(2)
C(17)-Mo(2)-C(20)	56.4(1)	C(18)-Mo(2)-C(20)	55.9(2)
C(19)-Mo(2)-C(20)	33.2(2)	C(6)-Mo(2)-C(21)	72.5(1)
C(7)-Mo(2)-C(21)	102.9(1)	C(8)-Mo(2)-C(21)	102.1(1)
C(16)-Mo(2)-C(21)	131.7(2)	C(17)-Mo(2)-C(21)	153.8(1)
C(18)-Mo(2)-C(21)	124.4(2)	C(19)-Mo(2)-C(21)	97.7(1)
C(20)-Mo(2)-C(21)	101.2(1)	C(6)-Mo(2)-C(22)	116.8(1)
C(7)-Mo(2)-C(22)	104.9(1)	C(8)-Mo(2)-C(22)	70.6(1)
C(16)-Mo(2)-C(22)	141.6(1)	C(17)-Mo(2)-C(22)	107.6(2)
C(18)-Mo(2)-C(22)	89.2(2)	C(19)-Mo(2)-C(22)	105.6(2)
C(20)-Mo(2)-C(22)	138.8(1)	C(21)-Mo(2)-C(22)	79.7(1)
Mo(1)-C(1)-O(1)	177.0(3)	Mo(1)-C(2)-O(2)	177.5(4)
Mo(1)-C(3)-H(3a)	118.4(14)	Mo(1)-C(3)-H(3b)	100.0(19)
H(3a)-C(3)-H(3b)	118.3(26)	Mo(1)-C(3)-C(4)	73.5(2)
H(3a)-C(3)-C(4)	118.7(17)	H(3b)-C(3)-C(4)	117.4(20)
Mo(1)-C(4)-C(3)	70.8(2)	Mo(1)-C(4)-C(5)	72.1(2)
C(3)-C(4)-C(5)	115.3(3)	Mo(1)-C(4)-C(6)	120.2(2)
C(3)-C(4)-C(6)	120.2(3)	C(5)-C(4)-C(6)	124.1(2)
Mo(1)-C(5)-C(4)	72.6(2)	Mo(1)-C(5)-H(5a)	103.2(15)
C(4)-C(5)-H(5a)	118.9(18)	Mo(1)-C(5)-H(5b)	123.3(18)
C(4)-C(5)-H(5b)	121.7(25)	H(5a)-C(5)-H(5b)	111.0(28)
Mo(2)-C(6)-C(4)	114.2(1)	Mo(2)-C(6)-H(6)	107.2(15)
C(4)-C(6)-H(6)	112.7(15)	Mo(2)-C(6)-C(7)	67.5(1)
C(4)-C(6)-C(7)	123.5(3)	H(6)-C(6)-C(7)	120.5(14)
Mo(2)-C(7)-C(6)	76.5(1)	Mo(2)-C(7)-H(7)	107.3(13)
C(6)-C(7)-H(7)	119.7(15)	Mo(2)-C(7)-C(8)	80.0(2)
C(6)-C(7)-C(8)	120.9(3)	H(7)-C(7)-C(8)	118.9(15)
Mo(2)-C(8)-C(7)	65.2(1)	Mo(2)-C(8)-C(9)	116.2(2)
C(7)-C(8)-C(9)	117.9(3)	Mo(2)-C(8)-C(10)	115.2(2)
C(7)-C(8)-C(10)	120.8(2)	Mo(1)-C(11)-C(12)	72.9(2)
Mo(1)-C(11)-C(15)	73.2(2)	C(12)-C(11)-C(15)	107.1(3)
Mo(1)-C(12)-C(11)	71.7(3)	Mo(1)-C(12)-C(13)	75.3(3)
C(11)-C(12)-C(13)	108.2(4)	Mo(1)-C(13)-C(12)	70.3(3)
Mo(1)-C(13)-C(14)	73.8(3)	C(12)-C(13)-C(14)	109.2(3)
Mo(1)-C(14)-C(13)	72.9(3)	Mo(1)-C(14)-C(15)	69.9(3)
C(13)-C(14)-C(15)	107.8(3)	Mo(1)-C(15)-C(11)	71.4(2)
Mo(1)-C(15)-C(14)	75.0(3)	C(11)-C(15)-C(14)	107.6(4)
Mo(2)-C(16)-C(17)	73.1(2)	Mo(2)-C(16)-C(20)	72.1(2)
C(17)-C(16)-C(20)	107.3(4)	Mo(2)-C(17)-C(16)	72.7(2)
Mo(2)-C(17)-C(18)	71.8(2)	C(16)-C(17)-C(18)	106.5(4)
Mo(2)-C(18)-C(17)	74.5(2)	Mo(2)-C(18)-C(19)	72.4(3)
C(17)-C(18)-C(19)	108.4(5)	Mo(2)-C(19)-C(18)	73.8(2)
Mo(2)-C(19)-C(20)	74.3(2)	C(18)-C(19)-C(20)	109.3(5)
Mo(2)-C(20)-C(16)	74.1(2)	Mo(2)-C(20)-C(19)	72.5(2)
C(16)-C(20)-C(19)	108.5(4)	Mo(2)-C(21)-O(3)	178.9(2)
Mo(2)-C(22)-O(4)	177.7(3)		

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	32(1)	42(1)	34(1)	4(1)	13(1)	-3(1)
Mo(2)	32(1)	27(1)	26(1)	1(1)	7(1)	-1(1)
O(1)	135(3)	117(3)	58(2)	-31(2)	57(2)	-37(2)
O(2)	85(2)	70(2)	87(2)	32(2)	5(2)	19(2)
O(3)	61(1)	42(1)	62(1)	-11(1)	26(1)	7(1)
O(4)	72(2)	93(2)	85(2)	27(2)	47(2)	-7(1)
C(1)	64(2)	56(2)	48(2)	-11(2)	22(2)	-17(2)
C(2)	48(2)	58(2)	49(2)	7(2)	10(2)	3(2)
C(3)	39(2)	38(1)	49(2)	9(1)	19(1)	2(1)
C(4)	29(1)	35(1)	32(1)	2(1)	8(1)	-1(1)
C(5)	47(2)	49(2)	36(2)	-2(1)	20(1)	-2(1)
C(6)	30(1)	31(1)	30(1)	0(1)	10(1)	0(1)
C(7)	32(1)	33(1)	31(1)	-0(1)	9(1)	3(1)
C(8)	41(2)	30(1)	28(1)	3(1)	5(1)	-0(1)
C(9)	58(2)	32(2)	52(2)	8(1)	11(2)	2(1)
C(10)	55(2)	54(2)	29(1)	4(1)	8(1)	-8(2)
C(11)	48(2)	104(3)	51(2)	9(2)	16(2)	-31(2)
C(12)	41(2)	109(3)	67(2)	4(2)	30(2)	-11(2)
C(13)	54(2)	113(4)	45(2)	12(2)	20(2)	-29(2)
C(14)	64(2)	78(3)	86(3)	35(2)	30(2)	-13(2)
C(15)	97(3)	64(2)	102(3)	-15(2)	67(3)	-41(2)
C(16)	61(2)	155(4)	29(2)	-30(2)	13(2)	4(3)
C(17)	141(4)	34(2)	37(2)	-9(1)	-15(2)	14(2)
C(18)	77(3)	146(5)	40(2)	-10(3)	5(2)	-58(3)
C(19)	85(3)	109(4)	41(2)	-13(2)	-12(2)	47(3)
C(20)	124(4)	53(2)	27(2)	4(1)	6(2)	-22(2)
C(21)	34(1)	38(1)	37(1)	5(1)	14(1)	3(1)
C(22)	45(2)	46(2)	49(2)	10(1)	17(1)	-3(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(3a)	2897(27)	1104(19)	2066(19)	39(7)
H(3b)	2569(30)	1084(21)	3074(23)	51(9)
H(5a)	1733(27)	2430(18)	3622(19)	41(8)
H(5b)	1457(35)	3344(21)	3016(24)	65(10)
H(6)	2815(23)	2577(16)	1228(17)	24(6)
H(7)	2704(22)	4180(15)	2294(16)	20(6)
H(9a)	4389	5601	1239	56
H(9b)	3749	5553	2046	56
H(9c)	2835	5651	943	56
H(10a)	3294	3395	173	61
H(10b)	3964	4299	7	61
H(10c)	2435	4282	-168	61
H(11)	-2510	1177	950	81
H(12)	-1950	2101	2510	79
H(13)	-39	1334	3814	84
H(14)	678	-14	3090	86
H(15)	-843	-127	1297	90
H(16)	4100	3772	4186	85
H(17)	5479	5052	3862	79
H(18)	7544	4338	3762	101
H(19)	7431	2675	4002	90
H(20)	5356	2319	4269	79

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	6740(1)	3281(1)	6201(1)	24(1)*
Mo(2)	4274(1)	2650(1)	7300(1)	25(1)*
O(1)	3896(5)	2506(3)	4992(2)	74(1)*
O(2)	3594(3)	4862(2)	6454(2)	53(1)*
O(3)	2693(3)	1836(2)	6861(1)	42(1)*
C(1)	4952(5)	2772(3)	5444(2)	42(1)*
C(2)	4486(4)	4046(3)	6566(2)	32(1)*
C(3)	6957(4)	2203(2)	7226(2)	28(1)*
C(4)	7921(4)	1671(2)	6665(2)	31(1)*
C(5)	7102(4)	1263(3)	5994(2)	34(1)*
C(6)	5472(5)	524(3)	5994(2)	42(1)*
C(7)	8317(5)	997(3)	5367(2)	50(1)*
C(10)	9786(10)	3789(8)	6020(7)	60(4)*
C(11)	9106(13)	4508(9)	6556(6)	59(4)*
C(12)	7648(11)	5141(6)	6268(6)	64(4)*
C(13)	7467(10)	4810(6)	5524(4)	50(3)*
C(14)	8680(16)	4027(9)	5373(6)	61(4)*
C(30)	7885(17)	4455(10)	5290(7)	62(4)*
C(31)	7365(11)	5067(6)	5879(5)	52(3)*
C(32)	8380(11)	4823(6)	6518(5)	52(3)*
C(33)	9616(13)	4039(9)	6330(7)	58(4)*
C(34)	9244(12)	3799(9)	5568(7)	57(4)*
C(20)	5128(6)	2766(4)	8611(2)	57(1)*
C(21)	3417(8)	2324(4)	8534(2)	73(2)*
C(22)	2309(6)	3137(5)	8231(2)	75(2)*
C(23)	3328(7)	4062(4)	8095(2)	66(2)*
C(24)	5076(6)	3836(4)	8352(2)	57(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-Mo(2)	2.881(1)	Mo(1)-C(1)	1.963(4)
Mo(1)-C(2)	2.060(3)	Mo(1)-C(3)	2.267(3)
Mo(1)-C(4)	2.284(3)	Mo(1)-C(5)	2.492(3)
Mo(1)-C(10)	2.396(8)	Mo(1)-C(11)	2.374(10)
Mo(1)-C(12)	2.356(8)	Mo(1)-C(13)	2.300(7)
Mo(1)-C(14)	2.318(12)	Mo(1)-C(30)	2.368(12)
Mo(1)-C(31)	2.295(7)	Mo(1)-C(32)	2.292(8)
Mo(1)-C(33)	2.338(10)	Mo(1)-C(34)	2.328(10)
Mo(2)-O(3)	1.705(2)	Mo(2)-C(2)	2.161(3)
Mo(2)-C(3)	2.088(3)	Mo(2)-C(20)	2.426(4)
Mo(2)-C(21)	2.383(4)	Mo(2)-C(22)	2.363(5)
Mo(2)-C(23)	2.365(4)	Mo(2)-C(24)	2.434(4)
O(1)-C(1)	1.153(5)	O(2)-C(2)	1.205(4)
C(3)-H(3)	0.919(30)	C(3)-C(4)	1.426(4)
C(4)-H(4)	1.024(43)	C(4)-C(5)	1.420(4)
C(5)-C(6)	1.512(5)	C(5)-C(7)	1.522(5)
C(10)-C(11)	1.416(15)	C(10)-C(14)	1.427(15)
C(10)-C(32)	1.893(13)	C(10)-C(33)	0.655(17)
C(10)-C(34)	0.894(16)	C(11)-C(12)	1.411(13)
C(11)-C(31)	1.868(13)	C(11)-C(32)	0.664(13)
C(11)-C(33)	0.807(16)	C(11)-C(34)	1.990(16)
C(12)-C(13)	1.403(13)	C(12)-C(30)	1.969(16)
C(12)-C(31)	0.729(13)	C(12)-C(32)	0.793(12)
C(12)-C(33)	1.986(13)	C(13)-C(14)	1.350(14)
C(13)-C(30)	0.689(15)	C(13)-C(31)	0.721(12)
C(13)-C(32)	1.890(12)	C(13)-C(34)	1.806(12)
C(14)-C(30)	0.797(17)	C(14)-C(31)	1.866(14)
C(14)-C(33)	1.832(17)	C(14)-C(34)	0.602(15)
C(30)-C(31)	1.370(15)	C(30)-C(34)	1.366(16)
C(31)-C(32)	1.382(12)	C(32)-C(33)	1.380(13)
C(33)-C(34)	1.422(17)	C(20)-C(21)	1.386(7)
C(20)-C(24)	1.379(6)	C(21)-C(22)	1.383(7)
C(22)-C(23)	1.384(7)	C(23)-C(24)	1.392(7)

(IV)

Table 3. Bond angles (°)

Mo(2)-Mo(1)-C(1)	87.7(1)	Mo(2)-Mo(1)-C(2)	48.4(1)
C(1)-Mo(1)-C(2)	80.0(1)	Mo(2)-Mo(1)-C(3)	46.0(1)
C(1)-Mo(1)-C(3)	114.0(1)	C(2)-Mo(1)-C(3)	91.3(1)
Mo(2)-Mo(1)-C(4)	76.6(1)	C(1)-Mo(1)-C(4)	103.0(1)
C(2)-Mo(1)-C(4)	125.0(1)	C(3)-Mo(1)-C(4)	36.5(1)
Mo(2)-Mo(1)-C(5)	85.4(1)	C(1)-Mo(1)-C(5)	70.3(1)
C(2)-Mo(1)-C(5)	125.9(1)	C(3)-Mo(1)-C(5)	63.4(1)
C(4)-Mo(1)-C(5)	34.2(1)	Mo(2)-Mo(1)-C(10)	143.8(3)
C(1)-Mo(1)-C(10)	127.2(3)	C(2)-Mo(1)-C(10)	136.5(2)
C(3)-Mo(1)-C(10)	103.3(3)	C(4)-Mo(1)-C(10)	85.3(2)
C(5)-Mo(1)-C(10)	96.9(2)	Mo(2)-Mo(1)-C(11)	118.2(3)
C(1)-Mo(1)-C(11)	149.0(3)	C(2)-Mo(1)-C(11)	104.0(3)
C(3)-Mo(1)-C(11)	96.8(3)	C(4)-Mo(1)-C(11)	99.6(3)
C(5)-Mo(1)-C(11)	124.8(3)	C(10)-Mo(1)-C(11)	34.5(4)
Mo(2)-Mo(1)-C(12)	114.3(2)	C(1)-Mo(1)-C(12)	121.4(2)
C(2)-Mo(1)-C(12)	77.9(2)	C(3)-Mo(1)-C(12)	120.1(3)
C(4)-Mo(1)-C(12)	133.9(2)	C(5)-Mo(1)-C(12)	156.1(2)
C(10)-Mo(1)-C(12)	59.2(3)	C(11)-Mo(1)-C(12)	34.7(3)
Mo(2)-Mo(1)-C(13)	139.2(2)	C(1)-Mo(1)-C(13)	93.1(2)
C(2)-Mo(1)-C(13)	91.5(2)	C(3)-Mo(1)-C(13)	157.9(2)
C(4)-Mo(1)-C(13)	141.9(2)	C(5)-Mo(1)-C(13)	132.9(2)
C(10)-Mo(1)-C(13)	57.9(3)	C(11)-Mo(1)-C(13)	56.4(3)
C(12)-Mo(1)-C(13)	35.0(3)	Mo(2)-Mo(1)-C(14)	172.4(3)
C(1)-Mo(1)-C(14)	95.7(3)	C(2)-Mo(1)-C(14)	125.4(3)
C(3)-Mo(1)-C(14)	137.0(3)	C(4)-Mo(1)-C(14)	109.1(3)
C(5)-Mo(1)-C(14)	102.1(3)	C(10)-Mo(1)-C(14)	35.2(4)
C(11)-Mo(1)-C(14)	56.5(4)	C(12)-Mo(1)-C(14)	58.1(4)
C(13)-Mo(1)-C(14)	34.0(3)	Mo(2)-Mo(1)-C(30)	154.8(3)
C(1)-Mo(1)-C(30)	87.8(3)	C(2)-Mo(1)-C(30)	108.4(3)
C(3)-Mo(1)-C(30)	154.3(3)	C(4)-Mo(1)-C(30)	128.5(3)
C(5)-Mo(1)-C(30)	116.1(3)	C(10)-Mo(1)-C(30)	51.1(4)
C(11)-Mo(1)-C(30)	61.4(4)	C(12)-Mo(1)-C(30)	49.3(4)
C(13)-Mo(1)-C(30)	16.9(4)	C(14)-Mo(1)-C(30)	19.6(4)
Mo(2)-Mo(1)-C(31)	124.8(2)	C(1)-Mo(1)-C(31)	105.1(2)
C(2)-Mo(1)-C(31)	80.6(2)	C(3)-Mo(1)-C(31)	138.0(2)
C(4)-Mo(1)-C(31)	145.0(2)	C(5)-Mo(1)-C(31)	149.7(2)
C(10)-Mo(1)-C(31)	61.1(3)	C(11)-Mo(1)-C(31)	47.1(3)
C(12)-Mo(1)-C(31)	18.0(3)	C(13)-Mo(1)-C(31)	18.0(3)
C(14)-Mo(1)-C(31)	47.7(4)	C(30)-Mo(1)-C(31)	34.1(4)
Mo(2)-Mo(1)-C(32)	113.3(2)	C(1)-Mo(1)-C(32)	140.1(2)
C(2)-Mo(1)-C(32)	89.3(2)	C(3)-Mo(1)-C(32)	104.5(2)
C(4)-Mo(1)-C(32)	114.4(2)	C(5)-Mo(1)-C(32)	141.0(2)
C(10)-Mo(1)-C(32)	47.6(3)	C(11)-Mo(1)-C(32)	16.2(3)
C(12)-Mo(1)-C(32)	19.6(3)	C(13)-Mo(1)-C(32)	48.6(3)
C(14)-Mo(1)-C(32)	60.0(4)	C(30)-Mo(1)-C(32)	58.5(4)
C(31)-Mo(1)-C(32)	35.1(3)	Mo(2)-Mo(1)-C(33)	130.7(3)
C(1)-Mo(1)-C(33)	141.6(3)	C(2)-Mo(1)-C(33)	123.6(3)
C(3)-Mo(1)-C(33)	96.7(3)	C(4)-Mo(1)-C(33)	87.9(3)
C(5)-Mo(1)-C(33)	107.1(3)	C(10)-Mo(1)-C(33)	15.8(4)
C(11)-Mo(1)-C(33)	19.7(4)	C(12)-Mo(1)-C(33)	30.1(3)
C(13)-Mo(1)-C(33)	59.7(3)	C(14)-Mo(1)-C(33)	46.3(4)
C(30)-Mo(1)-C(33)	58.1(4)	C(31)-Mo(1)-C(33)	57.1(3)
C(32)-Mo(1)-C(33)	34.7(3)	Mo(2)-Mo(1)-C(34)	165.6(3)
C(1)-Mo(1)-C(34)	106.2(3)	C(2)-Mo(1)-C(34)	136.6(3)
C(3)-Mo(1)-C(34)	122.1(3)	C(4)-Mo(1)-C(34)	96.1(3)
C(5)-Mo(1)-C(34)	95.5(3)	C(10)-Mo(1)-C(34)	21.8(4)
C(11)-Mo(1)-C(34)	30.1(4)	C(12)-Mo(1)-C(34)	42.0(3)
C(13)-Mo(1)-C(34)	45.9(3)	C(14)-Mo(1)-C(34)	14.9(4)
C(30)-Mo(1)-C(34)	33.8(4)	C(31)-Mo(1)-C(34)	56.1(3)
C(32)-Mo(1)-C(34)	58.0(3)	C(33)-Mo(1)-C(34)	35.5(4)
Mo(1)-Mo(2)-O(3)	106.6(1)	Mo(1)-Mo(2)-C(2)	45.5(1)
O(3)-Mo(2)-C(2)	103.7(1)	Mo(1)-Mo(2)-C(3)	51.3(1)
O(3)-Mo(2)-C(3)	117.7(1)	C(2)-Mo(2)-C(3)	93.7(1)
Mo(1)-Mo(2)-C(20)	120.8(1)	O(3)-Mo(2)-C(20)	129.1(1)
C(2)-Mo(2)-C(20)	122.0(1)	C(3)-Mo(2)-C(20)	82.6(1)
Mo(1)-Mo(2)-C(21)	154.2(1)	O(3)-Mo(2)-C(21)	97.3(1)
C(2)-Mo(2)-C(21)	137.3(1)	C(3)-Mo(2)-C(21)	108.7(2)
C(20)-Mo(2)-C(21)	33.5(2)	Mo(1)-Mo(2)-C(22)	150.1(1)
O(3)-Mo(2)-C(22)	92.0(1)	C(2)-Mo(2)-C(22)	108.0(2)
C(3)-Mo(2)-C(22)	138.1(1)	C(20)-Mo(2)-C(22)	55.5(2)
C(21)-Mo(2)-C(22)	33.9(2)	Mo(1)-Mo(2)-C(23)	116.6(1)
O(3)-Mo(2)-C(23)	118.7(1)	C(2)-Mo(2)-C(23)	80.7(1)
C(3)-Mo(2)-C(23)	123.0(1)	C(20)-Mo(2)-C(23)	55.8(1)
C(21)-Mo(2)-C(23)	56.6(1)	C(22)-Mo(2)-C(23)	34.0(2)
Mo(1)-Mo(2)-C(24)	103.9(1)	O(3)-Mo(2)-C(24)	147.5(1)
C(2)-Mo(2)-C(24)	89.7(1)	C(3)-Mo(2)-C(24)	90.2(1)
C(20)-Mo(2)-C(24)	33.0(1)	C(21)-Mo(2)-C(24)	55.6(1)
C(22)-Mo(2)-C(24)	55.5(2)	C(23)-Mo(2)-C(24)	33.7(2)
Mo(1)-C(1)-O(1)	177.9(3)	Mo(1)-C(2)-Mo(2)	86.0(1)
Mo(1)-C(2)-O(2)	140.3(3)	Mo(2)-C(2)-O(2)	133.6(2)
Mo(1)-C(3)-Mo(2)	82.7(1)	Mo(1)-C(3)-H(3)	117.0(19)
Mo(2)-C(3)-H(3)	116.5(20)	Mo(1)-C(3)-C(4)	72.4(2)
Mo(2)-C(3)-C(4)	133.1(2)	H(3)-C(3)-C(4)	110.2(20)
Mo(1)-C(4)-C(3)	71.1(2)	Mo(1)-C(4)-H(4)	111.7(24)
C(3)-C(4)-H(4)	119.9(23)	Mo(1)-C(4)-C(5)	80.9(2)
C(3)-C(4)-C(5)	123.6(3)	H(4)-C(4)-C(5)	115.7(23)
Mo(1)-C(5)-C(4)	64.8(2)	Mo(1)-C(5)-C(6)	119.2(2)
C(4)-C(5)-C(6)	121.3(3)	Mo(1)-C(5)-C(7)	113.1(2)
C(4)-C(5)-C(7)	117.6(3)	Mo(1)-C(10)-C(11)	71.9(5)
Mo(1)-C(10)-C(14)	69.4(6)	C(11)-C(10)-C(14)	102.9(8)
Mo(1)-C(10)-C(32)	63.3(3)	C(11)-C(10)-C(32)	16.2(5)
C(14)-C(10)-C(32)	86.7(7)	Mo(1)-C(10)-C(33)	77.0(11)
C(11)-C(10)-C(33)	16.0(11)	C(14)-C(10)-C(33)	118.5(14)
C(32)-C(10)-C(33)	31.8(11)	Mo(1)-C(10)-C(34)	74.8(8)
C(11)-C(10)-C(34)	117.1(11)	C(14)-C(10)-C(34)	14.3(8)
C(32)-C(10)-C(34)	100.9(9)	C(33)-C(10)-C(34)	132.6(16)
C(10)-H(10)-C(33)	25.6(7)	C(10)-H(10)-C(34)	32.5(6)
C(33)-H(10)-C(34)	58.1(7)	Mo(1)-C(11)-C(10)	73.6(5)
Mo(1)-C(11)-C(12)	71.9(5)	C(10)-C(11)-C(12)	112.3(9)
Mo(1)-C(11)-C(31)	64.2(4)	C(10)-C(11)-C(31)	92.2(7)
C(12)-C(11)-C(31)	20.1(5)	Mo(1)-C(11)-C(32)	74.9(11)
C(10)-C(11)-C(32)	127.1(15)	C(12)-C(11)-C(32)	15.8(10)
C(31)-C(11)-C(32)	35.5(11)	Mo(1)-C(11)-C(33)	77.6(10)
C(10)-C(11)-C(33)	12.9(10)	C(12)-C(11)-C(33)	124.9(14)
C(31)-C(11)-C(33)	104.8(13)	C(32)-C(11)-C(33)	119.3(19)
Mo(1)-C(11)-C(34)	63.8(4)	C(10)-C(11)-C(34)	73.6(5)
C(12)-C(11)-C(34)	88.7(7)	C(31)-C(11)-C(34)	68.6(5)
C(32)-C(11)-C(34)	103.6(13)	C(33)-C(11)-C(34)	16.3(10)
C(11)-H(11)-C(32)	27.2(6)	C(11)-H(11)-C(33)	31.9(6)
C(32)-H(11)-C(33)	59.1(7)	Mo(1)-C(12)-C(11)	73.4(5)
Mo(1)-C(12)-C(13)	70.3(4)	C(11)-C(12)-C(13)	103.5(8)
Mo(1)-C(12)-C(30)	65.7(4)	C(11)-C(12)-C(30)	89.9(7)
C(13)-C(12)-C(30)	13.6(5)	Mo(1)-C(12)-C(31)	74.3(8)
C(11)-C(12)-C(31)	118.0(12)	C(13)-C(12)-C(31)	14.5(7)
C(30)-C(12)-C(31)	28.1(8)	Mo(1)-C(12)-C(32)	75.7(8)
C(11)-C(12)-C(32)	13.2(8)	C(13)-C(12)-C(32)	116.1(11)
C(30)-C(12)-C(32)	102.5(10)	C(31)-C(12)-C(32)	130.5(14)
Mo(1)-C(12)-C(33)	64.5(4)	C(11)-C(12)-C(33)	19.5(6)
C(13)-C(12)-C(33)	84.1(6)	C(30)-C(12)-C(33)	70.5(6)
C(31)-C(12)-C(33)	98.6(10)	C(32)-C(12)-C(33)	32.1(9)
C(12)-H(12)-C(31)	27.3(5)	C(12)-H(12)-C(32)	29.5(5)
C(31)-H(12)-C(32)	56.8(6)	Mo(1)-C(13)-C(12)	74.4(5)
Mo(1)-C(13)-C(14)	73.7(6)	C(12)-C(13)-C(14)	111.2(8)
Mo(1)-C(13)-C(30)	87.1(12)	C(12)-C(13)-C(30)	117.9(13)
C(14)-C(13)-C(30)	26.8(12)	Mo(1)-C(13)-C(31)	80.6(8)
C(12)-C(13)-C(31)	14.7(8)	C(14)-C(13)-C(31)	125.9(11)
C(30)-C(13)-C(31)	152.6(16)	Mo(1)-C(13)-C(32)	65.5(3)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	24(1)	21(1)	27(1)	4(1)	2(1)	-1(1)
Mo(2)	25(1)	21(1)	29(1)	-0(1)	5(1)	-0(1)
O(1)	92(2)	55(2)	70(2)	-1(2)	-47(2)	-4(2)
O(2)	46(1)	38(1)	78(2)	21(1)	14(1)	18(1)
O(3)	34(1)	39(1)	53(1)	-5(1)	6(1)	-10(1)
C(1)	50(2)	30(2)	45(2)	4(1)	-8(2)	2(1)
C(2)	30(1)	27(1)	38(2)	5(1)	3(1)	2(1)
C(3)	28(1)	26(1)	29(1)	5(1)	1(1)	4(1)
C(4)	28(1)	26(1)	40(2)	9(1)	7(1)	7(1)
C(5)	43(2)	25(1)	34(2)	4(1)	9(1)	6(1)
C(6)	51(2)	29(2)	46(2)	-8(1)	8(2)	-1(1)
C(7)	65(2)	41(2)	45(2)	-1(2)	22(2)	10(2)
C(10)	18(3)	42(4)	120(10)	17(6)	9(4)	-5(3)
C(11)	42(7)	64(7)	70(6)	12(5)	-9(5)	-31(5)
C(12)	58(5)	29(3)	109(9)	-16(4)	41(5)	-24(3)
C(13)	46(4)	43(4)	60(6)	26(4)	-12(4)	-18(3)
C(14)	79(8)	59(7)	49(6)	-1(5)	36(6)	-26(5)
C(30)	79(8)	63(8)	45(5)	13(6)	16(6)	-22(6)
C(31)	51(4)	19(3)	86(7)	11(4)	18(4)	0(3)
C(32)	55(6)	37(4)	65(5)	-13(4)	15(4)	-28(5)
C(33)	22(4)	50(6)	103(10)	28(6)	-2(5)	-7(4)
C(34)	33(5)	50(5)	91(8)	20(6)	34(5)	-5(4)
C(20)	77(3)	65(3)	29(2)	-9(2)	1(2)	29(2)
C(21)	138(5)	47(2)	38(2)	-5(2)	39(3)	-32(3)
C(22)	44(2)	131(5)	50(2)	-24(3)	22(2)	-0(3)
C(23)	100(4)	50(2)	50(2)	-0(2)	27(2)	34(2)
C(24)	69(3)	53(2)	49(2)	-28(2)	15(2)	-20(2)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2 a^{*2} U_{11} + \ldots + 2hka^*b^* U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(3)	7733(41)	2431(24)	7606(17)	24(8)
H(4)	9292(57)	1685(35)	6692(23)	63(13)
H(6a)	4796	631	6426	46
H(6b)	5952	-210	5997	46
H(6c)	4704	627	5557	46
H(7a)	7736	1205	4902	48
H(7b)	8572	221	5363	48
H(7c)	9415	1402	5441	48
H(10)	10802	3303	6050	48
H(11)	9715	4609	7032	48
H(12)	7034	5709	6525	48
H(13)	6537	5138	5211	48
H(14)	8737	3652	4907	48
H(30)	7437	4489	4783	48
H(31)	6373	5569	5829	48
H(32)	8123	5039	7013	48
H(33)	10413	3660	6677	48
H(34)	9861	3262	5284	48
H(20)	6174	2390	8812	69
H(21)	3066	1591	8664	65
H(22)	1038	3077	8132	80
H(23)	2908	4735	7866	62
H(24)	6072	4336	8347	62

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Mo(1)	1870(1)	1309(1)	1088(1)	27(1)*
Mo(2)	1863(1)	1150(1)	2939(1)	28(1)*
Mo(3)	1052(1)	2709(1)	2108(1)	29(1)*
O(1)	-1705(4)	1359(2)	-70(2)	63(1)*
O(2)	5554(4)	870(3)	2766(3)	77(2)*
O(3)	4758(5)	2790(2)	3162(3)	74(2)*
O(4)	2539(6)	3302(2)	567(3)	79(2)*
C(1)	-383(6)	1349(3)	373(3)	41(2)*
C(2)	4124(7)	1000(3)	2696(3)	46(2)*
C(3)	3386(6)	2699(3)	2777(3)	47(2)*
C(4)	2052(6)	2975(3)	1126(3)	47(2)*
C(5)	111(5)	1636(2)	1822(2)	26(1)*
C(6)	-622(5)	1086(3)	2176(3)	33(1)*
C(7)	-167(5)	329(3)	2151(3)	36(1)*
C(8)	-962(7)	-353(3)	2491(3)	52(2)*
C(9)	1236(6)	310(2)	1749(3)	34(1)*
C(11)	3964(7)	1737(4)	338(4)	74(3)*
C(12)	4684(7)	1188(5)	646(4)	82(3)*
C(13)	3865(11)	533(4)	654(6)	96(4)*
C(14)	2531(8)	661(4)	-50(4)	89(3)*
C(15)	2630(8)	1443(5)	-238(3)	83(3)*
C(21)	693(7)	1163(4)	4192(3)	62(2)*
C(22)	1518(8)	489(3)	4169(3)	64(2)*
C(23)	3239(8)	629(3)	4229(3)	63(2)*
C(24)	3471(7)	1431(3)	4280(3)	59(2)*
C(25)	1879(7)	1763(3)	4272(3)	54(2)*
C(31)	-1616(6)	3063(3)	1970(4)	56(2)*
C(32)	-993(7)	3636(3)	1612(3)	52(2)*
C(33)	236(7)	3955(3)	2280(3)	50(2)*
C(34)	152(7)	3564(3)	3051(3)	53(2)*
C(35)	-1099(7)	3012(3)	2860(4)	55(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Mo(1)-Mo(2)	2.929(1)	Mo(1)-Mo(3)	3.079(1)
Mo(1)-C(1)	1.942(4)	Mo(1)-C(5)	2.079(4)
Mo(1)-C(9)	2.151(4)	Mo(1)-C(11)	2.367(7)
Mo(1)-C(12)	2.383(6)	Mo(1)-C(13)	2.313(9)
Mo(1)-C(14)	2.275(7)	Mo(1)-C(15)	2.302(6)
Mo(2)-Mo(3)	3.049(1)	Mo(2)-C(2)	1.954(5)
Mo(2)-C(5)	2.200(4)	Mo(2)-C(6)	2.263(4)
Mo(2)-C(7)	2.346(4)	Mo(2)-C(9)	2.361(4)
Mo(2)-C(21)	2.350(6)	Mo(2)-C(22)	2.322(5)
Mo(2)-C(23)	2.305(5)	Mo(2)-C(24)	2.304(4)
Mo(2)-C(25)	2.358(5)	Mo(3)-C(3)	1.969(5)
Mo(3)-C(4)	1.937(5)	Mo(3)-C(5)	2.048(4)
Mo(3)-C(31)	2.363(5)	Mo(3)-C(32)	2.336(5)
Mo(3)-C(33)	2.315(5)	Mo(3)-C(34)	2.326(5)
Mo(3)-C(35)	2.346(6)	O(1)-C(1)	1.154(5)
O(2)-C(2)	1.159(6)	O(3)-C(3)	1.164(6)
O(4)-C(4)	1.181(7)	C(5)-C(6)	1.405(6)
C(6)-H(6)	0.934(47)	C(6)-C(7)	1.435(6)
C(7)-C(8)	1.504(7)	C(7)-C(9)	1.403(7)
C(9)-H(9)	1.004(42)	C(11)-C(12)	1.314(10)
C(11)-C(15)	1.365(8)	C(12)-C(13)	1.332(12)
C(13)-C(14)	1.403(10)	C(14)-C(15)	1.411(11)
C(21)-C(22)	1.392(9)	C(21)-C(25)	1.366(8)
C(22)-C(23)	1.395(9)	C(23)-C(24)	1.420(8)
C(24)-C(25)	1.408(8)	C(31)-C(32)	1.364(8)
C(31)-C(35)	1.410(8)	C(32)-C(33)	1.411(7)
C(33)-C(34)	1.409(7)	C(34)-C(35)	1.386(7)

Table 3. Bond angles (°)

Mo(2)-Mo(1)-Mo(3)	60.9(1)	Mo(2)-Mo(1)-C(1)	113.4(1)
Mo(3)-Mo(1)-C(1)	90.1(1)	Mo(2)-Mo(1)-C(5)	48.5(1)
Mo(3)-Mo(1)-C(5)	41.4(1)	C(1)-Mo(1)-C(5)	69.5(2)
Mo(2)-Mo(1)-C(9)	52.7(1)	Mo(3)-Mo(1)-C(9)	107.7(1)
C(1)-Mo(1)-C(9)	91.5(2)	C(5)-Mo(1)-C(9)	72.8(2)
Mo(2)-Mo(1)-C(11)	132.0(1)	Mo(3)-Mo(1)-C(11)	104.7(2)
C(1)-Mo(1)-C(11)	112.1(2)	C(5)-Mo(1)-C(11)	145.3(2)
C(9)-Mo(1)-C(11)	139.6(2)	Mo(2)-Mo(1)-C(12)	109.8(1)
Mo(3)-Mo(1)-C(12)	117.6(2)	C(1)-Mo(1)-C(12)	136.3(2)
C(5)-Mo(1)-C(12)	152.7(2)	C(9)-Mo(1)-C(12)	109.2(2)
C(11)-Mo(1)-C(12)	32.1(2)	Mo(2)-Mo(1)-C(13)	112.1(2)
Mo(3)-Mo(1)-C(13)	149.1(2)	C(1)-Mo(1)-C(13)	118.4(2)
C(5)-Mo(1)-C(13)	156.6(2)	C(9)-Mo(1)-C(13)	84.7(3)
C(11)-Mo(1)-C(13)	55.4(3)	C(12)-Mo(1)-C(13)	32.9(3)
Mo(2)-Mo(1)-C(14)	141.6(2)	Mo(3)-Mo(1)-C(14)	156.7(2)
C(1)-Mo(1)-C(14)	84.2(2)	C(5)-Mo(1)-C(14)	150.3(2)
C(9)-Mo(1)-C(14)	95.1(2)	C(11)-Mo(1)-C(14)	57.6(2)
C(12)-Mo(1)-C(14)	56.7(2)	C(13)-Mo(1)-C(14)	35.6(3)
Mo(2)-Mo(1)-C(15)	165.0(1)	Mo(3)-Mo(1)-C(15)	120.9(2)
C(1)-Mo(1)-C(15)	81.7(2)	C(5)-Mo(1)-C(15)	144.0(2)
C(9)-Mo(1)-C(15)	130.8(2)	C(11)-Mo(1)-C(15)	34.0(2)
C(12)-Mo(1)-C(15)	55.4(2)	C(13)-Mo(1)-C(15)	57.6(3)
C(14)-Mo(1)-C(15)	35.9(3)	Mo(1)-Mo(2)-Mo(3)	62.0(1)
Mo(1)-Mo(2)-C(2)	68.5(1)	Mo(3)-Mo(2)-C(2)	99.6(2)
Mo(1)-Mo(2)-C(5)	45.1(1)	Mo(3)-Mo(2)-C(5)	42.2(1)
C(2)-Mo(2)-C(5)	111.9(2)	Mo(1)-Mo(2)-C(6)	70.5(1)
Mo(3)-Mo(2)-C(6)	73.4(1)	C(2)-Mo(2)-C(6)	136.2(2)
C(5)-Mo(2)-C(6)	36.7(2)	Mo(1)-Mo(2)-C(7)	70.7(1)
Mo(3)-Mo(2)-C(7)	104.9(1)	C(2)-Mo(2)-C(7)	113.3(2)
C(5)-Mo(2)-C(7)	62.9(1)	C(6)-Mo(2)-C(7)	36.2(2)
Mo(1)-Mo(2)-C(9)	46.5(1)	Mo(3)-Mo(2)-C(9)	103.0(1)
C(2)-Mo(2)-C(9)	79.8(2)	C(5)-Mo(2)-C(9)	66.7(1)
C(6)-Mo(2)-C(9)	61.0(2)	C(7)-Mo(2)-C(9)	34.7(2)
Mo(1)-Mo(2)-C(21)	156.0(1)	Mo(3)-Mo(2)-C(21)	104.5(2)
C(2)-Mo(2)-C(21)	135.4(2)	C(5)-Mo(2)-C(21)	111.2(2)
C(6)-Mo(2)-C(21)	86.9(2)	C(7)-Mo(2)-C(21)	96.0(2)
C(9)-Mo(2)-C(21)	128.6(2)	Mo(1)-Mo(2)-C(22)	154.4(1)
Mo(3)-Mo(2)-C(22)	139.1(1)	C(2)-Mo(2)-C(22)	111.5(2)
C(5)-Mo(2)-C(22)	134.2(2)	C(6)-Mo(2)-C(22)	99.1(2)
C(7)-Mo(2)-C(22)	87.0(2)	C(9)-Mo(2)-C(22)	107.9(2)
C(21)-Mo(2)-C(22)	34.7(2)	Mo(1)-Mo(2)-C(23)	145.1(2)
Mo(3)-Mo(2)-C(23)	139.5(1)	C(2)-Mo(2)-C(23)	79.2(2)
C(5)-Mo(2)-C(23)	168.8(2)	C(6)-Mo(2)-C(23)	133.9(2)
C(7)-Mo(2)-C(23)	112.8(2)	C(9)-Mo(2)-C(23)	116.3(2)
C(21)-Mo(2)-C(23)	58.1(2)	C(22)-Mo(2)-C(23)	35.1(2)
Mo(1)-Mo(2)-C(24)	141.4(1)	Mo(3)-Mo(2)-C(24)	103.7(1)
C(2)-Mo(2)-C(24)	80.2(2)	C(5)-Mo(2)-C(24)	143.8(2)
C(6)-Mo(2)-C(24)	143.6(2)	C(7)-Mo(2)-C(24)	145.6(2)
C(9)-Mo(2)-C(24)	148.8(2)	C(21)-Mo(2)-C(24)	58.1(2)
C(22)-Mo(2)-C(24)	58.7(2)	C(23)-Mo(2)-C(24)	35.9(2)
Mo(1)-Mo(2)-C(25)	147.4(1)	Mo(3)-Mo(2)-C(25)	86.3(1)
C(2)-Mo(2)-C(25)	113.2(2)	C(5)-Mo(2)-C(25)	115.2(2)
C(6)-Mo(2)-C(25)	109.4(2)	C(7)-Mo(2)-C(25)	129.3(2)
C(9)-Mo(2)-C(25)	162.8(2)	C(21)-Mo(2)-C(25)	34.2(2)
C(22)-Mo(2)-C(25)	57.7(2)	C(23)-Mo(2)-C(25)	58.5(2)
C(24)-Mo(2)-C(25)	35.1(2)	Mo(1)-Mo(3)-Mo(2)	57.1(1)
Mo(1)-Mo(3)-C(3)	89.5(1)	Mo(2)-Mo(3)-C(3)	70.1(1)
Mo(1)-Mo(3)-C(4)	67.0(1)	Mo(2)-Mo(3)-C(4)	118.1(1)
C(3)-Mo(3)-C(4)	85.7(2)	Mo(1)-Mo(3)-C(5)	42.1(1)
Mo(2)-Mo(3)-C(5)	46.1(1)	C(3)-Mo(3)-C(5)	112.5(2)
C(4)-Mo(3)-C(5)	103.9(2)	Mo(1)-Mo(3)-C(31)	117.9(1)
Mo(2)-Mo(3)-C(31)	113.5(1)	C(3)-Mo(3)-C(31)	150.1(2)
C(4)-Mo(3)-C(31)	114.7(2)	C(5)-Mo(3)-C(31)	84.7(2)
Mo(1)-Mo(3)-C(32)	126.2(1)	Mo(2)-Mo(3)-C(32)	147.7(1)
C(3)-Mo(3)-C(32)	136.3(2)	C(4)-Mo(3)-C(32)	86.7(2)
C(5)-Mo(3)-C(32)	111.1(2)	C(31)-Mo(3)-C(32)	34.2(2)
Mo(1)-Mo(3)-C(33)	155.6(1)	Mo(2)-Mo(3)-C(33)	147.1(1)
C(3)-Mo(3)-C(33)	102.1(2)	C(4)-Mo(3)-C(33)	92.2(2)
C(5)-Mo(3)-C(33)	142.5(2)	C(31)-Mo(3)-C(33)	57.8(2)
C(32)-Mo(3)-C(33)	35.3(2)	Mo(1)-Mo(3)-C(34)	167.0(1)
Mo(2)-Mo(3)-C(34)	111.8(1)	C(3)-Mo(3)-C(34)	92.8(2)
C(4)-Mo(3)-C(34)	125.9(2)	C(5)-Mo(3)-C(34)	125.8(2)
C(31)-Mo(3)-C(34)	57.7(2)	C(32)-Mo(3)-C(34)	58.4(2)
C(33)-Mo(3)-C(34)	35.4(2)	Mo(1)-Mo(3)-C(35)	134.4(1)
Mo(2)-Mo(3)-C(35)	96.0(1)	C(3)-Mo(3)-C(35)	117.1(2)
C(4)-Mo(3)-C(35)	144.5(2)	C(5)-Mo(3)-C(35)	92.3(2)
C(31)-Mo(3)-C(35)	34.8(2)	C(32)-Mo(3)-C(35)	57.9(2)
C(33)-Mo(3)-C(35)	58.1(2)	C(34)-Mo(3)-C(35)	34.6(2)
Mo(1)-C(1)-O(1)	178.0(4)	Mo(2)-C(2)-O(2)	163.1(4)
Mo(3)-C(3)-O(3)	171.6(4)	Mo(3)-C(4)-O(4)	164.6(4)
Mo(1)-C(5)-Mo(2)	86.4(1)	Mo(1)-C(5)-Mo(3)	96.5(2)
Mo(2)-C(5)-Mo(3)	91.7(1)	Mo(1)-C(5)-C(6)	120.6(3)
Mo(2)-C(5)-C(6)	74.1(2)	Mo(3)-C(5)-C(6)	136.5(3)
Mo(2)-C(6)-C(5)	69.2(2)	Mo(2)-C(6)-H(6)	118.0(24)
C(5)-C(6)-H(6)	125.4(27)	Mo(2)-C(6)-C(7)	75.0(2)
C(5)-C(6)-C(7)	113.4(4)	H(6)-C(6)-C(7)	120.8(27)
Mo(2)-C(7)-C(6)	68.8(2)	Mo(2)-C(7)-C(8)	127.1(3)
C(6)-C(7)-C(8)	122.9(4)	Mo(2)-C(7)-C(9)	73.3(2)
C(6)-C(7)-C(9)	111.6(4)	C(8)-C(7)-C(9)	125.5(4)
Mo(1)-C(9)-Mo(2)	80.8(1)	Mo(1)-C(9)-C(7)	119.3(3)
Mo(2)-C(9)-C(7)	72.1(2)	Mo(1)-C(9)-H(9)	125.4(25)
Mo(2)-C(9)-H(9)	121.2(21)	C(7)-C(9)-H(9)	115.1(25)
Mo(1)-C(11)-C(12)	74.6(4)	Mo(1)-C(11)-C(15)	70.4(4)
C(12)-C(11)-C(15)	109.0(6)	Mo(1)-C(12)-C(11)	73.2(4)
Mo(1)-C(12)-C(13)	70.6(5)	C(11)-C(12)-C(13)	110.7(6)
Mo(1)-C(13)-C(12)	76.5(5)	Mo(1)-C(13)-C(14)	70.7(5)
C(12)-C(13)-C(14)	108.2(7)	Mo(1)-C(14)-C(13)	73.7(5)
Mo(1)-C(14)-C(15)	73.1(4)	C(13)-C(14)-C(15)	104.8(6)
Mo(1)-C(15)-C(11)	75.6(4)	Mo(1)-C(15)-C(14)	71.0(4)
C(11)-C(15)-C(14)	107.3(5)	Mo(2)-C(21)-C(22)	71.6(3)
Mo(2)-C(21)-C(25)	73.2(3)	C(22)-C(21)-C(25)	108.7(5)
Mo(2)-C(22)-C(21)	73.8(3)	Mo(2)-C(22)-C(23)	71.8(3)
C(21)-C(22)-C(23)	108.5(5)	Mo(2)-C(23)-C(22)	73.1(3)
Mo(2)-C(23)-C(24)	72.0(3)	C(22)-C(23)-C(24)	107.3(5)
Mo(2)-C(24)-C(23)	72.1(3)	Mo(2)-C(24)-C(25)	74.5(3)
C(23)-C(24)-C(25)	107.5(5)	Mo(2)-C(25)-C(21)	72.5(3)
Mo(2)-C(25)-C(24)	70.3(3)	C(21)-C(25)-C(24)	108.0(5)
Mo(3)-C(31)-C(32)	71.9(3)	Mo(3)-C(31)-C(35)	71.9(3)
C(32)-C(31)-C(35)	108.4(4)	Mo(3)-C(32)-C(31)	73.9(3)
Mo(3)-C(32)-C(33)	71.4(3)	C(31)-C(32)-C(33)	107.9(4)
Mo(3)-C(33)-C(32)	73.3(3)	Mo(3)-C(33)-C(34)	72.8(3)
C(32)-C(33)-C(34)	107.7(4)	Mo(3)-C(34)-C(33)	71.9(3)
Mo(3)-C(34)-C(35)	73.5(3)	C(33)-C(34)-C(35)	108.0(4)
Mo(3)-C(35)-C(31)	73.3(3)	Mo(3)-C(35)-C(34)	71.9(3)
C(31)-C(35)-C(34)	108.1(5)		

Table 4. Anisotropic thermal parameters ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	25(1)	33(1)	23(1)	-3(1)	7(1)	-0(1)
Mo(2)	27(1)	33(1)	24(1)	-0(1)	6(1)	-1(1)
Mo(3)	31(1)	28(1)	29(1)	-4(1)	6(1)	-1(1)
O(1)	41(2)	87(3)	53(2)	4(2)	-14(2)	-3(2)
O(2)	28(2)	133(4)	70(3)	17(3)	12(2)	14(2)
O(3)	49(2)	82(3)	82(3)	10(2)	-11(2)	-23(2)
O(4)	106(3)	63(3)	83(3)	19(2)	58(3)	0(2)
C(1)	48(3)	43(3)	33(2)	-2(2)	10(2)	-4(2)
C(2)	40(3)	64(3)	35(2)	-3(2)	10(2)	-1(2)
C(3)	47(3)	42(3)	46(3)	-2(2)	2(2)	-11(2)
C(4)	56(3)	43(3)	49(3)	-1(2)	23(2)	2(2)
C(5)	25(2)	35(2)	24(2)	-4(2)	4(2)	-1(2)
C(6)	22(2)	43(3)	36(2)	-2(2)	10(2)	-7(2)
C(7)	33(2)	37(2)	38(2)	-2(2)	7(2)	-9(2)
C(8)	56(3)	41(3)	59(3)	-2(2)	17(3)	-20(2)
C(9)	39(3)	26(2)	35(2)	-3(2)	5(2)	0(2)
C(11)	69(4)	75(4)	98(5)	-9(4)	66(4)	-7(3)
C(12)	39(4)	162(8)	52(3)	10(4)	23(3)	16(4)
C(13)	114(7)	82(5)	129(7)	48(5)	102(6)	65(5)
C(14)	101(5)	108(5)	60(4)	-61(4)	72(4)	-44(4)
C(15)	56(4)	167(7)	34(3)	39(4)	28(3)	35(4)
C(21)	59(4)	98(5)	35(3)	-1(3)	23(2)	2(3)
C(22)	101(5)	58(3)	34(3)	6(2)	17(3)	-22(3)
C(23)	89(4)	67(4)	29(3)	11(2)	0(3)	22(3)
C(24)	66(4)	66(4)	22(2)	-1(2)	-1(2)	-16(3)
C(25)	61(4)	57(3)	25(2)	-4(2)	15(2)	5(3)
C(31)	30(3)	57(3)	61(4)	-33(3)	10(3)	7(2)
C(32)	61(4)	51(3)	40(3)	-2(2)	2(2)	25(3)
C(33)	63(4)	29(2)	56(3)	-7(2)	9(3)	-1(2)
C(34)	65(4)	49(3)	41(3)	-17(2)	-0(2)	22(3)
C(35)	62(4)	45(3)	66(4)	-7(3)	40(3)	8(3)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(6)	-1701(54)	1190(24)	2467(27)	46(13)
H(6a)	-1483	-220	2968	63
H(6b)	-85	-720	2678	63
H(6c)	-1795	-565	2033	63
H(9)	1810(50)	-198(24)	1758(25)	32(11)
H(11)	4319	2259	367	89
H(12)	5666	1251	1298	96
H(13)	4138	55	945	114
H(14)	1733	296	-344	104
H(15)	1666	1719	-664	91
H(21)	-500	1246	4157	65
H(22)	983	-2	4115	74
H(23)	4107	253	4239	72
H(24)	4519	1699	4312	68
H(25)	1653	2297	4315	62
H(31)	-2720	2753	1666	66
H(32)	-1227	3791	1016	63
H(33)	997	4362	2219	56
H(34)	835	3664	3611	63
H(35)	-1410	2655	3263	64

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Rh(1)	3260(1)	1360(1)	1154(1)	22(1)*
Rh(2)	1909(1)	767(1)	1821(1)	20(1)*
O(1)	3884(4)	370(7)	2661(3)	37(2)*
O(2)	2402(5)	3427(7)	2672(3)	48(2)*
C(1)	3317(5)	701(8)	2145(4)	24(2)*
C(2)	2359(5)	2837(9)	2102(4)	31(3)*
C(3)	2694(6)	3384(9)	1475(4)	33(3)*
C(4)	1811(5)	3310(9)	848(4)	31(3)*
C(5)	1978(7)	4050(9)	172(4)	39(3)*
C(6)	890(6)	3965(10)	995(5)	42(3)*
C(7)	1830(5)	1679(8)	841(4)	23(2)*
C(10)	3701(6)	1157(11)	88(4)	39(3)*
C(11)	3181(7)	1593(13)	-647(4)	57(4)*
C(12)	4361(6)	1955(10)	576(4)	39(3)*
C(13)	4707(7)	3492(11)	475(6)	61(4)*
C(14)	4792(5)	1038(9)	1143(4)	29(3)*
C(15)	5604(6)	1372(12)	1767(5)	50(4)*
C(16)	4352(5)	-359(9)	1022(4)	30(3)*
C(17)	4600(6)	-1653(10)	1467(5)	42(3)*
C(18)	3655(5)	-257(10)	367(4)	33(3)*
C(19)	3056(7)	-1447(11)	6(6)	55(4)*
C(20)	1566(5)	-1590(8)	2064(4)	21(2)*
C(21)	2163(6)	-2677(9)	2019(4)	35(3)*
C(22)	1602(5)	-714(9)	2691(4)	26(3)*
C(23)	2240(6)	-949(10)	3412(4)	36(3)*
C(24)	897(5)	372(9)	2523(4)	27(3)*
C(25)	664(6)	1468(10)	3030(5)	40(3)*
C(26)	411(5)	190(9)	1788(4)	30(3)*
C(27)	-472(6)	919(11)	1427(5)	44(3)*
C(28)	831(5)	-1065(8)	1512(4)	26(2)*
C(29)	525(6)	-1653(10)	766(4)	37(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Rh(1)-Rh(2)	2.624(2)	Rh(1)-C(1)	1.988(8)
Rh(1)-C(3)	2.191(9)	Rh(1)-C(7)	2.059(7)
Rh(1)-C(10)	2.286(9)	Rh(1)-C(12)	2.231(9)
Rh(1)-C(14)	2.253(6)	Rh(1)-C(16)	2.303(6)
Rh(1)-C(18)	2.292(9)	Rh(2)-C(1)	2.010(7)
Rh(2)-C(2)	2.065(8)	Rh(2)-C(7)	2.050(6)
Rh(2)-C(20)	2.312(7)	Rh(2)-C(22)	2.283(6)
Rh(2)-C(24)	2.231(8)	Rh(2)-C(26)	2.231(8)
Rh(2)-C(28)	2.303(7)	O(1)-C(1)	1.189(8)
O(2)-C(2)	1.215(10)	C(2)-C(3)	1.485(12)
C(3)-C(4)	1.566(10)	C(3)-H(3)	1.116(103)
C(4)-C(5)	1.535(12)	C(4)-C(6)	1.552(13)
C(4)-C(7)	1.513(11)	C(7)-H(7)	0.887(59)
C(10)-C(11)	1.510(11)	C(10)-C(12)	1.419(11)
C(10)-C(18)	1.425(13)	C(12)-C(13)	1.529(14)
C(12)-C(14)	1.415(11)	C(14)-C(15)	1.524(11)
C(14)-C(16)	1.442(11)	C(16)-C(17)	1.474(12)
C(16)-C(18)	1.444(10)	C(18)-C(19)	1.484(13)
C(20)-C(21)	1.505(11)	C(20)-C(22)	1.447(10)
C(20)-C(28)	1.425(9)	C(22)-C(23)	1.512(9)
C(22)-C(24)	1.425(11)	C(24)-C(25)	1.496(12)
C(24)-C(26)	1.452(10)	C(26)-C(27)	1.486(11)
C(26)-C(28)	1.466(12)	C(28)-C(29)	1.510(10)

(VI)

Table 3. Bond angles (°)

Rh(2)-Rh(1)-C(1)	49.4(2)	Rh(2)-Rh(1)-C(3)	71.1(2)
C(1)-Rh(1)-C(3)	86.3(3)	Rh(2)-Rh(1)-C(7)	50.2(2)
C(1)-Rh(1)-C(7)	99.1(3)	C(3)-Rh(1)-C(7)	82.6(3)
Rh(2)-Rh(1)-C(10)	143.6(2)	C(1)-Rh(1)-C(10)	151.0(3)
C(3)-Rh(1)-C(10)	121.2(3)	C(7)-Rh(1)-C(10)	102.0(3)
Rh(2)-Rh(1)-C(12)	177.6(2)	C(1)-Rh(1)-C(12)	132.0(3)
C(3)-Rh(1)-C(12)	106.7(3)	C(7)-Rh(1)-C(12)	126.2(3)
C(10)-Rh(1)-C(12)	36.6(3)	Rh(2)-Rh(1)-C(14)	145.2(2)
C(1)-Rh(1)-C(14)	97.3(3)	C(3)-Rh(1)-C(14)	123.2(3)
C(7)-Rh(1)-C(14)	102.9(3)	C(10)-Rh(1)-C(14)	81.0(3)
C(12)-Rh(1)-C(14)	36.8(3)	Rh(2)-Rh(1)-C(16)	121.0(2)
C(1)-Rh(1)-C(16)	90.2(3)	C(3)-Rh(1)-C(16)	159.0(3)
C(7)-Rh(1)-C(16)	138.1(3)	C(10)-Rh(1)-C(16)	66.8(3)
C(12)-Rh(1)-C(16)	81.4(3)	C(14)-Rh(1)-C(16)	36.9(3)
Rh(2)-Rh(1)-C(18)	120.4(2)	C(1)-Rh(1)-C(18)	117.9(3)
C(3)-Rh(1)-C(18)	155.4(3)	C(7)-Rh(1)-C(18)	106.3(3)
C(10)-Rh(1)-C(18)	36.3(3)	C(12)-Rh(1)-C(18)	81.2(3)
C(14)-Rh(1)-C(18)	81.3(3)	C(16)-Rh(1)-C(18)	36.8(3)
Rh(1)-Rh(2)-C(1)	48.6(2)	Rh(1)-Rh(2)-C(2)	72.8(2)
C(1)-Rh(2)-C(2)	72.8(3)	Rh(1)-Rh(2)-C(7)	50.5(2)
C(1)-Rh(2)-C(7)	98.8(3)	C(2)-Rh(2)-C(7)	79.0(3)
Rh(1)-Rh(2)-C(20)	120.8(2)	C(1)-Rh(2)-C(20)	99.0(3)
C(2)-Rh(2)-C(20)	153.7(3)	C(7)-Rh(2)-C(20)	127.2(3)
Rh(1)-Rh(2)-C(22)	140.2(2)	C(1)-Rh(2)-C(22)	95.7(3)
C(2)-Rh(2)-C(22)	117.9(3)	C(7)-Rh(2)-C(22)	100.8(3)
C(20)-Rh(2)-C(22)	36.7(3)	Rh(1)-Rh(2)-C(24)	172.1(2)
C(1)-Rh(2)-C(24)	124.5(3)	C(2)-Rh(2)-C(24)	102.0(3)
C(7)-Rh(2)-C(24)	135.3(3)	C(20)-Rh(2)-C(24)	81.8(3)
C(22)-Rh(2)-C(24)	36.8(3)	Rh(1)-Rh(2)-C(26)	149.8(2)
C(1)-Rh(2)-C(26)	157.7(3)	C(2)-Rh(2)-C(26)	119.0(3)
C(7)-Rh(2)-C(26)	102.1(3)	C(20)-Rh(2)-C(26)	81.9(3)
C(22)-Rh(2)-C(26)	82.3(3)	C(24)-Rh(2)-C(26)	36.0(3)
Rh(1)-Rh(2)-C(28)	124.8(2)	C(1)-Rh(2)-C(28)	130.5(3)
C(2)-Rh(2)-C(28)	156.2(3)	C(7)-Rh(2)-C(28)	99.5(3)
C(20)-Rh(2)-C(28)	36.0(2)	C(22)-Rh(2)-C(28)	81.1(3)
C(24)-Rh(2)-C(28)	82.3(3)	C(26)-Rh(2)-C(28)	37.7(3)
Rh(1)-C(1)-Rh(2)	82.0(3)	Rh(1)-C(1)-O(1)	139.8(6)
Rh(2)-C(1)-O(1)	138.3(6)	Rh(2)-C(2)-O(2)	127.5(6)
Rh(2)-C(2)-C(3)	104.2(5)	O(2)-C(2)-C(3)	128.1(6)
Rh(1)-C(3)-C(2)	96.3(5)	Rh(1)-C(3)-C(4)	92.3(5)
C(2)-C(3)-C(4)	104.8(7)	Rh(1)-C(3)-H(3)	112.4(64)
C(2)-C(3)-H(3)	111.0(61)	C(4)-C(3)-H(3)	131.9(57)
C(3)-C(4)-C(5)	112.5(7)	C(3)-C(4)-C(6)	116.1(7)
C(3)-C(4)-C(7)	92.1(6)	C(5)-C(4)-C(7)	115.7(7)
C(6)-C(4)-C(7)	114.3(7)	Rh(1)-C(7)-Rh(2)	79.4(2)
Rh(1)-C(7)-C(4)	99.2(5)	Rh(2)-C(7)-C(4)	113.8(5)
Rh(1)-C(7)-H(7)	127.3(41)	Rh(2)-C(7)-H(7)	122.3(41)
C(4)-C(7)-H(7)	110.4(38)	Rh(1)-C(10)-C(11)	129.7(7)
Rh(1)-C(10)-C(12)	69.6(5)	C(11)-C(10)-C(12)	126.4(9)
Rh(1)-C(10)-C(16)	72.1(5)	C(11)-C(10)-C(16)	123.1(8)
C(12)-C(10)-C(16)	108.2(7)	Rh(1)-C(12)-C(10)	73.8(5)
Rh(1)-C(12)-C(13)	125.1(7)	C(10)-C(12)-C(13)	126.4(8)
Rh(1)-C(12)-C(14)	72.5(5)	C(10)-C(12)-C(14)	108.6(8)
C(13)-C(12)-C(14)	124.6(7)	Rh(1)-C(14)-C(12)	70.8(5)
Rh(1)-C(14)-C(15)	124.7(6)	C(12)-C(14)-C(15)	126.0(8)
Rh(1)-C(14)-C(16)	73.4(4)	C(12)-C(14)-C(16)	108.3(8)
C(15)-C(14)-C(16)	123.6(7)	Rh(1)-C(16)-C(14)	69.7(4)
Rh(1)-C(16)-C(17)	126.1(6)	C(14)-C(16)-C(17)	126.3(8)
Rh(1)-C(16)-C(18)	71.3(5)	C(14)-C(16)-C(18)	108.8(7)
C(17)-C(16)-C(18)	126.9(7)	Rh(1)-C(18)-C(10)	71.8(5)
Rh(1)-C(18)-C(16)	72.1(5)	C(10)-C(18)-C(16)	108.0(7)
Rh(1)-C(18)-C(19)	126.3(6)	C(10)-C(18)-C(19)	125.3(7)
C(16)-C(18)-C(19)	126.4(8)	Rh(2)-C(20)-C(21)	125.7(5)
Rh(2)-C(20)-C(22)	70.5(4)	C(21)-C(20)-C(22)	125.3(8)
Rh(2)-C(20)-C(28)	71.7(4)	C(21)-C(20)-C(28)	126.1(8)
C(22)-C(20)-C(28)	108.5(8)	Rh(2)-C(22)-C(20)	72.7(4)
Rh(2)-C(22)-C(23)	125.7(5)	C(20)-C(22)-C(23)	126.2(7)
Rh(2)-C(22)-C(24)	69.6(4)	C(20)-C(22)-C(24)	108.2(8)
C(23)-C(22)-C(24)	125.5(7)	Rh(2)-C(24)-C(22)	73.6(5)
Rh(2)-C(24)-C(25)	123.8(6)	C(22)-C(24)-C(25)	125.8(8)
Rh(2)-C(24)-C(26)	71.0(4)	C(22)-C(24)-C(26)	108.4(7)
C(25)-C(24)-C(26)	125.7(7)	Rh(2)-C(26)-C(24)	71.0(4)
Rh(2)-C(26)-C(27)	130.2(6)	C(24)-C(26)-C(27)	126.8(8)
Rh(2)-C(26)-C(28)	73.8(4)	C(24)-C(26)-C(28)	107.0(8)
C(27)-C(26)-C(28)	125.2(7)	Rh(2)-C(28)-C(20)	72.4(4)
Rh(2)-C(28)-C(26)	66.5(4)	C(20)-C(28)-C(26)	107.8(8)
Rh(2)-C(28)-C(29)	124.0(6)	C(20)-C(28)-C(29)	127.4(7)
C(26)-C(28)-C(29)	124.7(8)		

Table 4. Anisotropic thermal parameters ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	19(1)	30(1)	18(1)	-1(1)	2(1)	-2(1)
Rh(2)	17(1)	25(1)	16(1)	-0(1)	1(1)	0(1)
O(1)	24(3)	53(4)	28(3)	10(3)	-4(2)	2(3)
O(2)	66(4)	43(4)	34(3)	-11(3)	7(3)	-9(3)
C(1)	19(4)	12(4)	38(4)	-4(3)	4(3)	0(3)
C(2)	32(4)	34(5)	26(4)	-10(4)	2(3)	3(4)
C(3)	38(5)	24(5)	35(4)	-6(3)	5(4)	-2(4)
C(4)	27(4)	40(5)	25(4)	-0(4)	0(3)	-5(4)
C(5)	47(5)	34(5)	32(5)	6(4)	-2(4)	-2(4)
C(6)	47(5)	41(6)	36(5)	11(4)	9(4)	12(4)
C(7)	16(3)	28(5)	25(4)	-6(3)	1(3)	-2(3)
C(10)	31(4)	67(7)	23(4)	-0(4)	12(3)	7(4)
C(11)	55(6)	91(9)	27(5)	3(5)	13(4)	22(6)
C(12)	31(4)	52(6)	39(5)	4(4)	20(4)	2(4)
C(13)	47(6)	59(7)	66(8)	14(6)	35(6)	-6(5)
C(14)	20(4)	37(5)	32(4)	-3(4)	6(3)	-1(3)
C(15)	22(4)	76(7)	51(6)	-15(5)	7(4)	-9(5)
C(16)	25(4)	35(5)	34(4)	1(4)	11(3)	6(4)
C(17)	41(5)	36(6)	53(6)	3(4)	16(4)	5(4)
C(18)	25(4)	44(5)	34(4)	-12(4)	11(3)	-1(4)
C(19)	35(5)	63(7)	66(7)	-31(6)	7(5)	-4(5)
C(20)	20(4)	21(4)	21(4)	2(3)	1(3)	-0(3)
C(21)	33(4)	36(5)	34(4)	4(4)	-1(4)	5(4)
C(22)	19(4)	44(5)	20(4)	6(3)	3(3)	-7(4)
C(23)	38(5)	49(6)	16(4)	2(4)	-3(3)	-5(4)
C(24)	25(4)	34(5)	26(4)	-5(3)	11(3)	-6(3)
C(25)	40(5)	45(6)	42(5)	-2(4)	22(4)	7(4)
C(26)	20(4)	42(5)	30(4)	9(4)	11(3)	-3(4)
C(27)	25(4)	59(6)	46(5)	9(5)	2(4)	5(4)
C(28)	24(4)	31(5)	20(4)	1(3)	1(3)	-6(3)
C(29)	32(4)	49(6)	25(4)	0(4)	-5(3)	-11(4)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(5a)	2551	3694	63	44
H(5b)	2021	5076	234	44
H(5c)	1459	3822	-211	44
H(6a)	840	3627	1457	50
H(6b)	365	3617	646	50
H(6c)	890	4999	992	50
H(11a)	3187	2604	-750	63
H(11b)	2542	1264	-716	63
H(11c)	3497	1075	-959	63
H(13a)	4264	4072	153	73
H(13b)	5275	3399	300	73
H(13c)	4846	3941	934	73
H(15a)	5634	2400	1820	63
H(15b)	6184	1024	1668	63
H(15c)	5503	941	2198	63
H(17a)	4776	-1253	1936	47
H(17b)	5120	-2182	1359	47
H(17c)	4073	-2287	1443	47
H(19a)	3172	-2281	307	71
H(19b)	3279	-1622	-421	71
H(19c)	2393	-1253	-113	71
H(21a)	2067	-3271	1549	40
H(21b)	2039	-3595	2339	40
H(21c)	2827	-2583	2171	40
H(23a)	2885	-1165	3409	36
H(23b)	1982	-1702	3653	36
H(23c)	2207	-50	3652	36
H(25a)	1202	1986	3284	48
H(25b)	434	840	3350	48
H(25c)	180	2138	2823	48
H(27a)	-626	1863	1571	53
H(27b)	-976	267	1448	53
H(27c)	-377	960	949	53
H(29a)	455	-695	421	38
H(29b)	-54	-2179	711	38
H(29c)	1019	-2292	702	38
H(3)	3249(60)	4222(116)	1633(58)	40(36)
H(7)	1450(41)	1344(65)	453(32)	40(14)

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
Re(1)	1939(1)	531(1)	1498(1)	31(1)*
Re(2)	2008(1)	-2429(1)	1287(1)	29(1)*
O(1)	918(13)	3569(11)	1320(7)	80(5)*
O(2)	1876(14)	663(14)	3073(5)	82(5)*
O(3)	-1707(11)	-310(12)	1205(6)	67(4)*
O(4)	5334(11)	1560(11)	1701(5)	56(4)*
O(5)	4392(13)	-5325(10)	1352(6)	69(4)*
O(6)	1663(12)	-2738(11)	2603(5)	62(4)*
O(7)	-356(11)	-3573(12)	534(5)	65(4)*
O(8)	6066(10)	-1454(11)	2189(5)	56(3)*
C(1)	1274(16)	2413(15)	1387(7)	47(5)*
C(2)	1851(16)	636(15)	2400(7)	48(5)*
C(3)	-438(16)	-36(14)	1319(7)	45(4)*
C(4)	4065(12)	1169(11)	1619(5)	27(3)*
C(5)	3804(16)	-4282(14)	1350(6)	45(4)*
C(6)	1945(14)	-2595(13)	2124(6)	40(4)*
C(7)	870(16)	-3139(14)	794(6)	43(4)*
C(8)	4885(13)	-1768(13)	1859(6)	36(4)*
C(9)	2139(12)	-500(12)	581(5)	32(4)*
C(10)	3642(13)	-1027(13)	461(5)	33(3)*
C(11)	3888(15)	-2285(13)	161(6)	39(4)*
C(12)	2659(17)	-2946(15)	-387(6)	49(5)*
C(13)	5578(15)	-2767(15)	122(7)	47(5)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Re(1)-Re(2)	3.058(1)	Re(1)-C(1)	1.889(15)
Re(1)-C(2)	1.948(13)	Re(1)-C(3)	2.003(13)
Re(1)-C(4)	1.983(11)	Re(1)-C(9)	2.109(11)
Re(2)-C(5)	1.947(14)	Re(2)-C(6)	1.963(13)
Re(2)-C(7)	1.982(12)	Re(2)-C(8)	1.979(11)
Re(2)-C(9)	2.353(11)	Re(2)-C(10)	2.281(11)
Re(2)-C(11)	2.404(13)	O(1)-C(1)	1.162(18)
O(2)-C(2)	1.141(17)	O(3)-C(3)	1.106(16)
O(4)-C(4)	1.138(14)	O(5)-C(5)	1.128(17)
O(6)-C(6)	1.097(17)	O(7)-C(7)	1.163(16)
O(8)-C(8)	1.136(14)	C(9)-H(9)	1.201(114)
C(9)-C(10)	1.441(16)	C(10)-H(10)	0.910(78)
C(10)-C(11)	1.385(18)	C(11)-C(12)	1.517(17)
C(11)-C(13)	1.519(19)		

Table 3. Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U
H(9)	857(135)	-664(130)	338(62)	47(36)
H(10)	4564(98)	-593(90)	633(43)	6(29)
H(12a)	1603	-2679	-740	59
H(12b)	2250	-3932	-348	59
H(12c)	2974	-2657	-830	59
H(13a)	5789	-3742	122	56
H(13b)	6468	-2608	530	56
H(13c)	5705	-2395	-256	56

(VII)

Table 3. Bond angles (°)

Re(2)-Re(1)-C(1)	164.9(4)	Re(2)-Re(1)-C(2)	103.4(4)
C(1)-Re(1)-C(2)	91.3(6)	Re(2)-Re(1)-C(3)	91.4(4)
C(1)-Re(1)-C(3)	91.1(6)	C(2)-Re(1)-C(3)	91.9(6)
Re(2)-Re(1)-C(4)	90.2(3)	C(1)-Re(1)-C(4)	86.4(5)
C(2)-Re(1)-C(4)	91.1(5)	C(3)-Re(1)-C(4)	176.2(5)
Re(2)-Re(1)-C(9)	50.2(3)	C(1)-Re(1)-C(9)	115.1(5)
C(2)-Re(1)-C(9)	153.6(5)	C(3)-Re(1)-C(9)	88.5(5)
C(4)-Re(1)-C(9)	89.9(4)	Re(1)-Re(2)-C(5)	168.1(3)
Re(1)-Re(2)-C(6)	77.7(4)	C(5)-Re(2)-C(6)	95.0(5)
Re(1)-Re(2)-C(7)	97.6(4)	C(5)-Re(2)-C(7)	91.1(5)
C(6)-Re(2)-C(7)	86.0(5)	Re(1)-Re(2)-C(8)	82.4(4)
C(5)-Re(2)-C(8)	88.2(5)	C(6)-Re(2)-C(8)	89.5(5)
C(7)-Re(2)-C(8)	175.4(5)	Re(1)-Re(2)-C(9)	43.5(3)
C(5)-Re(2)-C(9)	146.9(5)	C(6)-Re(2)-C(9)	116.2(5)
C(7)-Re(2)-C(9)	81.0(4)	C(8)-Re(2)-C(9)	102.0(4)
Re(1)-Re(2)-C(10)	70.3(3)	C(5)-Re(2)-C(10)	116.2(5)
C(6)-Re(2)-C(10)	147.8(5)	C(7)-Re(2)-C(10)	100.2(4)
C(8)-Re(2)-C(10)	84.2(4)	C(9)-Re(2)-C(10)	36.2(4)
Re(1)-Re(2)-C(11)	102.7(3)	C(5)-Re(2)-C(11)	85.5(5)
C(6)-Re(2)-C(11)	174.7(4)	C(7)-Re(2)-C(11)	88.7(5)
C(8)-Re(2)-C(11)	95.8(4)	C(9)-Re(2)-C(11)	62.4(4)
C(10)-Re(2)-C(11)	33.3(4)	Re(1)-C(1)-O(1)	179.6(11)
Re(1)-C(2)-O(2)	177.2(13)	Re(1)-C(3)-O(3)	177.5(12)
Re(1)-C(4)-O(4)	178.2(10)	Re(2)-C(5)-O(5)	174.9(13)
Re(2)-C(6)-O(6)	176.3(11)	Re(2)-C(7)-O(7)	175.2(11)
Re(2)-C(8)-O(8)	176.6(11)	Re(1)-C(9)-Re(2)	86.3(4)
Re(1)-C(9)-H(9)	108.1(59)	Re(2)-C(9)-H(9)	111.5(59)
Re(1)-C(9)-C(10)	123.1(7)	Re(2)-C(9)-C(10)	69.2(6)
H(9)-C(9)-C(10)	128.5(61)	Re(2)-C(10)-C(9)	74.7(6)
Re(2)-C(10)-H(10)	109.7(55)	C(9)-C(10)-H(10)	121.5(59)
Re(2)-C(10)-C(11)	81.8(8)	C(9)-C(10)-C(11)	125.8(11)
H(10)-C(10)-C(11)	112.3(60)	Re(2)-C(11)-C(10)	64.8(7)
Re(2)-C(11)-C(12)	107.9(8)	C(10)-C(11)-C(12)	122.4(11)
Re(2)-C(11)-C(13)	115.5(8)	C(10)-C(11)-C(13)	119.5(11)

Table 4. Anisotropic temperature factors ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re(1)	30(1)	29(1)	35(1)	-2(1)	4(1)	0(1)
Re(2)	29(1)	26(1)	30(1)	4(1)	3(1)	-1(1)
O(1)	56(7)	37(6)	135(11)	13(7)	-16(8)	7(5)
O(2)	95(9)	114(11)	37(6)	-3(6)	15(5)	0(8)
O(3)	34(5)	77(8)	87(8)	-5(6)	4(5)	-15(5)
O(4)	44(6)	51(6)	70(6)	-5(5)	2(4)	-10(5)
O(5)	79(8)	32(5)	96(8)	10(5)	13(6)	17(5)
O(6)	62(6)	75(8)	54(6)	21(5)	25(5)	-4(6)
O(7)	45(5)	67(7)	74(7)	-2(6)	-11(5)	-14(5)
O(8)	41(5)	63(7)	59(5)	9(5)	-8(4)	-3(5)
C(1)	49(8)	48(9)	45(7)	-6(6)	8(6)	-19(7)
C(2)	54(8)	47(8)	46(7)	-4(6)	13(6)	0(7)
C(3)	57(8)	29(7)	51(7)	-3(6)	9(6)	-4(6)
C(4)	27(6)	14(5)	40(6)	-8(4)	1(4)	-2(4)
C(5)	58(8)	42(8)	36(6)	1(6)	10(5)	-4(7)
C(6)	29(6)	48(8)	44(6)	5(6)	11(5)	-0(6)
C(7)	54(8)	32(7)	43(6)	7(5)	12(6)	-0(6)
C(8)	38(6)	32(6)	38(6)	14(5)	7(5)	-4(5)
C(9)	26(5)	40(7)	32(5)	4(5)	7(4)	7(5)
C(10)	32(5)	44(7)	24(5)	7(5)	7(4)	1(5)
C(11)	38(7)	41(7)	38(6)	3(5)	8(5)	5(6)
C(12)	65(9)	44(8)	35(6)	-7(6)	-0(6)	-17(7)
C(13)	41(7)	44(8)	57(8)	-6(6)	15(6)	7(6)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$